



# Understanding the origin of structure sensitivity in nano crystalline mixed Cu/Mg-AI oxides catalyst for low-pressure methanol synthesis

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Abstract: Cu nanoparticles of size 5-10 nm supported on Mg-Al mixed oxide were prepared by the sol-gel method. Cu loading was varied from 2.5 to 10 wt% onto support to investigate the effect on particle size and activity/selectivity of the catalyst. The Cu/Mg-Al catalysts containing small copper nanoparticles favor high selectivity of methanol, while the rate of CO formation was higher for larger copper particles. The high methanol selectivity (~99%) and methanol formation rate (0.016 mol  $g_{Cu}^{-1}$  h<sup>-1</sup>) over the 4.8Cu/Mg-Al catalyst was due to the combined effect of the presence of high Cu dispersion, Cu surface area, and strong interaction between small Cu particles with Mg-Al support. The high stability of the catalyst was attributed to the strong binding of the Cu cluster (-179.7 kJ/mol) to the MgO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, as shown by the DFT study. Additionally, the adsorption energy calculated using DFT showed preferential adsorption of CO2 and H<sub>2</sub> at the Cu/MgO(100) active site (-120.9 kJ/mol, -130.4 kJ/mol) compared to the Cu/γ-Al<sub>2</sub>O<sub>3</sub>(100) (-64.2 kJ/mol, -85.7 kJ/mol)active site. The high selectivity of the catalyst towards methanol can be attributed to the higher stability of the formate (HCOO) intermediate (-257.2 kJ/mol) compared to the carboxylate (COOH) intermediate (-131.0 kJ/mol).

## Introduction

Global atmosphere concentration of CO<sub>2</sub> has reached an unprecedented level of 400 ppm in recent times due to excessive use of fossil resources creating global warming and serious environmental problems <sup>1, 2</sup>. It has become imperative to adopt a circular economy through reduce, reuse, and recycle approaches, and significant thrusts are now being given to reducing CO<sub>2</sub> concentration through carbon capture and utilization (CCU) routes <sup>2-4</sup>. CO<sub>2</sub> is a non-toxic, cheap, and widely available C1 Feedstock that can be converted into important chemicals and fuels like methanol, dimethyl ether (DME), and synthetic natural gas (SNG) <sup>3-5</sup>. Therefore, chemical utilization of CO<sub>2</sub> has attracted great attention, which can reduce the effect of excess CO2 in the natural environment and transform the economy towards carbon neutrality. Catalytic conversion of CO<sub>2</sub> to methanol is especially becoming attractive because of the potential uses of methanol as both chemical feedstock and fuel and fuel components such as direct methanol fuel cells <sup>6-9</sup>. However, obtaining a high yield of methanol, i.e., high CO<sub>2</sub> conversion and high methanol selectivity, remains a major challenge due to thermodynamic difficulties in the  $CO_2$  activation <sup>10-13</sup> since  $CO_2$  is a very stable molecule ( $\Delta H^f$  = -393.5 kJ/mol  $CO_2(g)$ .

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> based catalyst prepared through conventional coprecipitation method is being used commercially in the production of methanol under the operating temperature of (473-573 K) and high pressure (7-10 MPa) <sup>1, 14, 15</sup>. Such a catalyst has also been investigated extensively for methanol synthesis from CO<sub>2</sub> hydrogenation <sup>16-18</sup>. However, low selectivity for methanol has been encountered in the CO<sub>2</sub> hydrogenation because of the large quantities of CO formation as a by-product <sup>19</sup>. Two competitive reactions which suppress CO<sub>2</sub> conversion to methanol are reverse water gas shift (RWGS) reaction for the formation of CO and also the formation of methane via hydrogenation through C-O bond dissociation <sup>20, 21</sup>. It has been shown that catalyst with moderate activity for non-selective RWGS reaction is suitable for high methanol selectivity <sup>22, 23</sup>. Although there is still significant doubt about the actual reaction mechanism, under specific industrial conditions, methanol is produced mostly through CO<sub>2</sub> hydrogenation, with CO acting as a CO<sub>2</sub> source and water producing oxygen atoms as a scavenger, which acts as an inhibitor of active metal sites <sup>24-27</sup>.

Most of the earlier studies report low conversion of CO2, poor catalytic stability, and low selectivity of methanol, where copper alone found ineffective to produce methanol via CO2 hydrogenation <sup>28, 29</sup>. It is also reported that single oxide support cannot improve the performance of the active Cu particles significantly, but the presence of second metal oxide such as MgO, ZrO<sub>2</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> can stabilize Cu nanoparticles <sup>30, 31</sup>. Arena et al. found that after the introduction of ZrO<sub>2</sub> in the Cu-ZnO catalyst prepared by different methods showed high activity for methanol production, and the stability of this catalyst was also improved <sup>26, 32</sup>. It is also reported that the presence of Ga also improved the activity and stability of the catalyst <sup>28, 33, 34</sup>. Schlögl et al. <sup>35</sup> showed the role of ZnO in the Cu/ZnO catalyst prepared by using a hydroxyl carbonate precursor. Based on the literature reports, it is generally accepted that the Cu<sup>0</sup> species in catalysts are the active phase for CO<sub>2</sub> hydrogenation, and the metal oxide supports can disperse the active copper species on the surface. On the other hand, the presence of H<sub>2</sub> favours the sintering of the Cu particles, which deactivates the catalyst. Typically, the Cu oxide of the synthesized catalyst is reduced by H<sub>2</sub> and CO during the reaction. Researchers also

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reported that the conversion of CO<sub>2</sub> is affected by the metallic Cu surface area, and the selectivity of methanol highly depends on the dispersion of basic sites on the catalyst surface <sup>36</sup>. So, the presence of high copper surface area and basicity of the catalyst is the key factors for selecting the methanol synthesis catalyst via CO<sub>2</sub> hydrogenation <sup>37</sup>. Dasireddy et al. <sup>38</sup>. reported the significant role of alkaline-earth metal oxide (MgO, BaO, SrO, and CaO) on the copper-based catalyst, which enhanced the number of CO2 and H2 adsorption active sites and also increased the metal-support interaction with high metallic Cu surface area. Ren et al. 39 showed that the presence of MgO increases the formation of small metallic copper species, which enhanced the catalytic activity of the Cu-based methanol synthesis catalyst.

In the current investigation, we have prepared highly dispersed sinter resistant Cu-nanoparticles in the range between 5-10 nm supported on nanocrystalline Mg-Al mixed oxide catalyst, which has been found to provide superior selectivity (~99%) methanol and moderate activity at low pressure (3 MPa) methanol synthesis. In addition, DFT was to used to understand the high stability and high methanol selectivity of Cu/MgO/Al<sub>2</sub>O<sub>3</sub> catalyst.

## **Results and Discussion**

Powder XRD pattern of all synthesized fresh catalyst are shown in Figures S1a to S1f, respectively (supporting information). Interestingly, the 2.3Cu/Mg-Al and 4.8Cu/Mg-Al catalyst exhibited no distinctive peaks of any Cu oxides in the XRD pattern (Figures S1c and S1d), suggesting the presence of a highly dispersed small nanocrystalline Cu-particles. It has to be noted that XRD has the limitations of analyzing the crystallites below 5 nm 40. Whereas, the 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalyst showed a peak at 38.75°, which is assigned for CuO (JCPDS Card no. 89-5896). The peak at 38.75° in the XRD pattern was used to determine the crystallite size of the CuO (111) phase using Scherrer's equation (Table S1, supporting information). Moreover, powder X-ray diffraction (XRD) patterns of the reduced and spent catalysts are presented in Figure 1A and 2B. All reduced Cu/Mg-Al catalysts showed uniformly resolved diffraction peaks. The 4.8Cu/Mg-Al does not show any Cu peaks due to very high Cu dispersion and presence of smaller Cu particles. The XRD peak at 20 value of 44.3° represents the metallic Cu (111). The intensity of any peak in the XRD pattern indicates the extent of crystallinity of a particular plane. The XRD peak at 44.3° for 4.8Cu/Al shows very intense because the metallic Cu species present in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support are highly crystalline in nature compare to the other supports. We believe that in presence of Mg the dispersion of Cu increases at the same time the Cu particles size also decreases, so the intensity of the Cu peaks decreases (crystallinity is low). In general, the smaller the particles the more is the XRD peak broadening and vice versa. However, in the XRD patterns of reduced 7.3Cu/Mg-Al and 9.6Cu/Mg-Al samples, an additional low intense peak at 43.31° can be seen for the (111) plane of Cu<sup>0</sup> species (JCPDS card no.89-2838). The peak at 43.31° in the XRD pattern was used to determine the crystallite size of the Cu (111) phase using Scherrer's equation (Table 1). The diffraction peaks at 20 values of 36.94°, 42.92°, 62.31°, and 78.64° are assigned to the diffraction from (111), (200), (220),

and (222) planes of magnesium oxide (MgO) (JCDPS card no.89-4248). In addition, it was observed that the diffraction peak for spinel species such as MgAl<sub>2</sub>O<sub>4</sub> (JCPDS No: 21-1152) and CuAl<sub>2</sub>O<sub>4</sub> (JCPDS No: 01-1153) was found, which exhibited the 20 values at 65.28° and 31.27° 40, 41. Low intensity for CuAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> spinel species suggest that the hydrotalcite-like precursor was converted into mixed metal oxide of both CuAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> spinel species due to the high dispersion of copper <sup>42</sup>. Furthermore, y-Al<sub>2</sub>O<sub>3</sub> was not found to be a distinct phase due to it is in amorphous materials. On the other hand, XRD analysis for the spent catalysts was carried out to check the crystallinity and the thermal stability of the catalysts after the reaction, and it was found that the spent catalysts did not show any major change in their crystallinity and phase behavior. However, the spent 9.6Cu/Mg-Al and 7.3Cu/Mg-Al catalysts showed metallic copper species at a 20 value of 44.31°. It was observed that due to high dispersion and smaller copper particle size resulted in inhibition in sintering through strong metal-support interaction between copper nanoparticles and MgO support in the 4.8Cu/Mg-Al catalyst during the reactions.



Figure 1. Powder XRD patterns of Figure (A) reduced, (B) spent, (C) Isotherm

plot and (D), BJH plot for 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts. The physicochemical properties of the reduced and used catalysts are given in Table1. The BET-Surface area of catalysts

was determined by N2 adsorption-desorption measurements. It can be seen that the sample exhibits a type-IV adsorptiondesorption isotherm with a type  $H_2$  hysteresis loop in the P/P<sub>0</sub> range from 0.80 to 0.95 (Figure 1). The pores are predominantly in the range from 2 to 12 nm as confirmed by the pore size distribution which is justified from the TEM images (inset of Figure. 2). The surface area is decreased when the amount of copper loading was increased. The surface area of the catalysts was different with different supports. The specific surface area of 4.8Cu/AI catalyst was 60 m²/g, whereas 4.8Cu/Mg catalyst has a The 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, surface area 64 m<sup>2</sup>/g. 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts exhibited surface area of 72, 70, 61, and 57 m<sup>2</sup>/g, respectively. It was found that when Cu loading was less than 5 wt% (in case of 2.3Cu/Mg-Al and 4.8Cu/Mg-Al) the catalyst does not show any deactivation and it

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is stable as shown in the time-on-steam study. But when the Cu loading was more than 5 wt% (in case of 7.3Cu/Mg-Al and 9.6Cu/Mg-Al) the catalysts deactivate with time. In the surface area analysis also, it was found that surface area of 2.3Cu/Mg-Al changes from 72 to 68.3 and for 4.8Cu/Mg-Al catalyst it changes from 70 to 67.8 m<sup>2</sup>/g during catalysis, whereas it changes from 61 to 50.3 m<sup>2</sup>/g for 7.3Cu/Mg-Al and for 9.6Cu/Mg-Al it changes to 42.5 from 57 m<sup>2</sup>/g during catalysis. BET analysis of spent 2.3Cu/Mg-Al and 4.8Cu/Mg-Al catalysts revealed that there was only a negligible change in surface area, indicating good thermal stability of the catalyst. Whereas, the spent 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts showed further decrease in surface area due to agglomeration of catalyst particles during catalysis.

Table 1: Physico-chemical properties of Cu/Mg-Al catalysts.

Sample	Cu loading (wt.%)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )		crys	Average tallite siz	e e <sup>a</sup> (nm)
		Reduced	Spent	Cu (111)	MgO (200)	γ-Al <sub>2</sub> O <sub>3</sub> (100)
MgO	0	76	ND	ND	ND	ND
γ-Al <sub>2</sub> O <sub>3</sub>	0	68	ND	ND	ND	ND
4.8Cu/Al	4.8	60	58.2	8.8	ND	27.5
4.8Cu/Mg	4.8	64	55.6	11.3	24.8	ND
2.3Cu/Mg-Al	2.3	72	68.3	ND	22.8	ND
4.8Cu/Mg-Al	4.8	70	67.8	ND	24.2	ND
7.3Cu/Mg-Al	7.3	61	50.3	9.2	24.8	ND
9.6Cu/Mg-Al	9.6	57	42.5	12.4	25.3	ND
ND- Not determined: a determined from XRD using Scherrer formula						

N<sub>2</sub>O titration method was carried out to find out Cu metal dispersion and Cu particle size in the reduced catalysts. It was found that with increasing Cu loading, the dispersion of Cu decreases gradually, and for 2.3Cu/Mg-AI, 4.8Cu/Mg-AI, 7.3Cu/Mg-AI, and 9.6Cu/Mg-AI catalysts, the dispersion values were 19.4%, 18.7%, 14.8%, and 11.8%, respectively. The maximum copper dispersion was found for the 4.8Cu/Mg-AI catalyst. The decreasing trend of metal dispersion was due to the formation of much bigger Cu particles with increasing Cu loading. The number of active particle sites estimated from metal dispersion analysis is provided in Table 2.

Table 2: Copper metal dispersion (MD) and Copper particle sizes obtained by the  $N_2O$  decomposition method.

Sample	Cu dispersion (%)	Cu SA (S <sub>Cu</sub> , m²g⁻¹)	Cu particle size (d <sub>cu</sub> , nm)	Number of the active Cu atoms/g
4.8Cu/Al	8.4	9.7	12.3	2.24 x 10 <sup>11</sup>
4.8Cu/Mg	10.6	12.3	9.7	6.87 x 10 <sup>12</sup>
2.3Cu/Mg-Al	19.4	21.6	5.3	2.97 x 10 <sup>15</sup>
4.8Cu/Mg-Al	18.7	20.8	5.5	5.90 x 10 <sup>15</sup>
7.3Cu/Mg-Al	14.8	17.1	6.8	1.10 x 10 <sup>14</sup>
9.6Cu/Mg-Al	11.8	14.2	8.7	3.78 x 10 <sup>13</sup>

TEM images of 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al are shown in Figure 2. Several black dots are seen in Figure 2, which may be attributed to Cu particles. The TEM images of 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts are showing agglomerated particles. This is maybe due to high Cu loading. As illustrated in Figure 2a, 2.3Cu/Mg-Al indicates the formation of about 6 nm metallic Cu species, which possessed a spherical

morphology. Whereas the 4.8Cu/Mg-Al catalyst showed around 7 nm of metallic Cu species, and the lattice fringes for Cu (111) with a d-spacing value of 2.08 nm can be seen. The TEM images of 7.3Cu/Mg-Al and 9.6Cu/Mg-Al showed 20-40 nm of MgO nanoparticles (Figure 2c and 2d). The dispersion of 4.8Cu/Mg-Al nanocrystalline catalysts was determined by the STEM elemental mapping, and the result indicates the homogenous distribution of Cu-nanoparticles on nanocrystalline Mg-Al support (Figure S4, supporting information). The morphologies of spent catalysts were also investigated by TEM analysis, and the images are shown in Figure 2e, 2f, 2g, and 2h, respectively. The 2.3Cu/Mg-Al, 4.8Cu/Mg-Al catalysts retained its spherical morphologies after catalysis (Figures 2e and 2f), whereas the 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts showed agglomerated particles after catalysis (Figures 2g and 2h). The analysis indicated that larger particles unable to resist sintering during catalysis.



Figure 2. TEM images of reduced and spent catalysts (a,e) 2.3Cu/Mg-Al, (b,f) 4.8Cu/Mg-Al, (c,g) 7.3Cu/Mg-Al and (d,h) 9.6Cu/Mg-Al.

The reduction profiles of all samples prepared with different loading of the amount of copper exhibit a broad peak of H<sub>2</sub> consumption in the range of 160-280 °C. The catalyst having lower Cu loading (2.3Cu/Mg-Al and 4.8Cu/Mg-Al catalysts) with smaller crystallites size of Cu showed the reduction at relatively lower temperatures compare to their higher Cu loading (7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts) counterparts. The lower temperature reduction peaks indicate the reduction of relatively smaller CuO particles, while the higher temperature peaks are attributed to the reduction of comparatively larger CuO particles <sup>43</sup>. From XRD analysis it was found that when Cu loading was less than 5 wt% XRD does not show any Cu peaks whereas when Cu loading was more than 5 wt%, in the XRD pattern different Cu species like CuO and Cu<sub>2</sub>Al<sub>2</sub>O<sub>4</sub> were present In addition, strong metal-support interaction is also present (Figure 3A), <sup>44, 45</sup>. The 2.3Cu/Mg-Al catalyst exhibited a single board reduction peak at 190 °C, which is attributed to the reduction of the Cu oxide species of the catalyst in Figure 3A and after deconvolution it shows two peaks at 174 and 196 °C (Figure S2, supporting information). We believe that the hightemperature reduction peak corresponds to the reduction of bulk CuO with relatively large particle size, while the low-temperature reduction peak corresponds to the reduction of dispersed CuO. On the other hand, 4.8Cu/Mg-Al catalyst showed two reduction peaks in the range 160-208 °C, which was ascribed into different aggregation states of CuO, Cu<sub>2</sub>O, and their combination

indicates different reduction properties of copper species <sup>2, 38, 46</sup>. The reduction peak at a lower temperature for 4.8Cu/Mg-Al catalyst indicates the higher dispersion of Cu species with strong metal-support interaction. In addition, with increasing copper loading, the 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts showed the reduction peak shift to higher temperatures. The 7.3Cu/Mg-Al catalysts exhibited the reduction temperature between 162 to 238 °C, while the 9.6Cu/Mg-Al catalysts exhibited the reduction temperature between 168 to 251 °C. The reduction peak for these two catalysts was shifted to higher temperatures due to the presence of larger (agglomerated) Cu particles with weak metal-support interaction. In addition, the reduction peak area increases with increasing Cu loading over Cu/Mg-Al catalysts. The total hydrogen consumption values (mmol/g) are 0.33963, 0.38936, 0.77511 and 0.92081 for 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al, respectively. The  $H_2$ consumption values during the TPR analysis in the Table S2 (supporting information). The reduction peak area for 4.8Cu/Mg is less than 2.3Cu/Mg-Al because the amount of reducible Cu species is less for 4.8Cu/Mg compare to 2.3Cu/Mg-Al. From Figure S3. (supporting information) the TEM analysis it was found that 4.8Cu/Mg catalyst produced agglomerated Cu species (big Cu particles) whereas 2.3Cu/Mg-Al catalyst produced highly dispersed Cu species (small Cu particles). As the amount of copper loading increased, the reduction peaks of agglomerated larger Cu particles were shifted to higher temperatures, which was not easily reduced in compare to smaller Cu particles during the reduction process.

The surface basicity as well as strength of interaction of CO<sub>2</sub> with the catalyst surface of various Cu/Mg-Al catalysts were examined by CO2-TPD. The CO2-TPD profile of Cu/Mg-AI catalysts (Figure 3B) exhibited three types of peaks, which are attributed to weak, moderate, and strong basic sites, respectively <sup>2, 46</sup>. As shown in Figure 3B, the low temperature (50-120 °C) peak corresponds to a weak basic site, which can occupy the adsorbed acidic CO<sub>2</sub> on the surface. The moderate basic sites at a temperature range between 120-200 °C may be assigned to metal-oxygen pair (Mg-O and Al-O) and surface oxygen anions, whereas the strongly basic site is appearing at the temperature between 200-250 °C due to the unsaturated O2ions and the lattice oxygen anions 38, 47, 48. The 4.8Cu/Mg-Al catalyst showed strong basic sites, and the reason may due to increasing the metal dispersion and copper surface area, which helps to increase the amount of basic sites of the catalyst <sup>39</sup>. In addition, the formation of CuAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> spinel phases can also increase the amount of basic sites. However, the significant increase in the basic sites in the 4.8Cu/Mg-Al catalyst is beneficial for the adsorption of CO<sub>2</sub>.

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Figure:3 (A)  $H_2\mbox{-}TPR$  patterns and (B)  $CO_2\mbox{-}TPD$  profile of synthesized catalysts.

X-ray photoelectron spectroscopic (XPS) analysis was carried out to examine the chemical state of Cu, Mg, Al and O present on the surface of the fresh, reduced (H<sub>2</sub> pre-treated) and spent 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts. The XPS spectra of the reduced catalysts are given in Figure 4, whereas the XPS spectra of the fresh and spent catalysts are given in Figures S5, (supporting information). Cu2p<sub>3/2</sub> XPS peaks of the fresh catalysts with binding energy values of 933.2 eV. 933.1 eV. 933.2 eV and 933.2 eV respectively, for 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalyst confirmed the presence of Cu<sup>2+</sup> in the sample. The Cu XPS spectra of the fresh 2.3Cu/Mg-Al. 4.8Cu/Mg-AI, 7.3Cu/Mg-AI and 9.6Cu/Mg-AI catalysts are shown in Figure S5 (supporting information). All the catalysts showed peaks at ~933.1 eV for the Cu2p<sub>3/2</sub> and peaks near ~953.1 eV for the Cu  $2p_{1/2},$  followed by shake-up satellite peak at ~942 eV and 962 eV, confirming the presence of Cu<sup>2+</sup>. These satellites were due to the charge transfer between the transition metal 3d and surrounding ligand oxygen 2p orbitals, and the reduced and spent catalyst also showed the absence of satellites in the spectra, confirmed that no considerable quantity of Cu2+ species is present on the surface 49. All the catalysts (2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al) showed Cu2p<sub>3/2</sub> binding values ~932.2 eV and Cu2p\_{1/2} binding energy values of ~ 952 eV  $^{\rm 50\text{-}53}$  confirming the presence of metallic Cu after the reduction as shown in Table 3 (supporting information). The Mg 2p XPS spectra for 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts contain binding energy peaks at 50.8, 51.0, 51.1, and 51.2 eV, respectively, indicating that the Mg species exist as Mg<sup>2+</sup> (Figure 4B). Moreover, the XPS spectra of Al 2p (Figure 4C) in all the synthesized catalysts are found in the binding energy value of ~74.7 eV confirming that AI is present as Al3+ in the prepared catalysts and the results are summarized in Table 3 (Figure 4C). The O1s XPS spectra(Figure 4D) for 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts show two types of peaks, whereas peak near 530 eV (529.8, 530.0, 530.3 and 530.3 eV, respectively for 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al) belongs to lattice O (Mg-O and Cu-O), whereas the peak near 531eV (531.3, 531.4, 531.1 and 531.0 eV, respectively for 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al) is due to the presence of O-H in the catalysts 53-55. The XPS spectra of spent 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts are shown in Figure S5 (Supporting information) and (Table 3). For all spent Cu-containing samples showing Cu 2p<sub>3/2</sub>

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binding energy peaks at ~ 932.2 eV and Cu  $2p_{1/2}$  binding energy peaks at ~ 952 eV  $^{53\cdot55}$  as shown in Table 3.



Figure 4. XPS analysis of 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and. 6Cu/Mg-Al catalysts. (A) Cu 2p (reduced), (B) Mg 2p (reduced), (C) Al 2p (reduced), and (D) O 1s (reduced).

Table 3: Binding energy/kinetic energy of peaks in the XPS spectra.

MgO-y-Al<sub>2</sub>O<sub>3</sub> support also plays a crucial role for the high methanol selectivity and catalyst stability. Additionally, y-Al<sub>2</sub>O<sub>3</sub> acts as a stabilizer for the Cu-particles preventing the Cuparticles against sintering during reaction when Cu loading was less than 5wt%. The Cu/MgO interface has been proposed to generate the active site responsible for the high CH<sub>3</sub>OH selectivity 56. The Cu/MgO interface has been proposed to generate the active site responsible for the high CH<sub>3</sub>OH selectivity 56. So, y-Al<sub>2</sub>O<sub>3</sub> acts as a stabilizer for the Cu/MgO catalyst against sintering during catalysis as observed by earlier researchers also <sup>30, 56</sup>. The conversion of CO<sub>2</sub> and high yield of methanol was found over 4.8Cu/Mg-Al catalyst at a lower temperature (200 °C) compared to 2.3Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts. The lowest conversion of CO2 was found for the 9.6Cu/Mg-Al catalyst due to the presence of less number of active sites for the adsorption of reactive molecules during catalysis. When copper loading was increased, Cu dispersion decreased, and CO<sub>2</sub> conversion was also decreased. The catalyst 4.8Cu/Mg-Al exhibited 19.4% of Cu dispersion, while the 2.3Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalyst showed dispersion value of 18.7, 14.8, and 11.8%, respectively.

Samples	Cu 2p/eV			Mg 2p/eV	Al 2p/eV	O 1s/eV	
	Reduced		Spe	Spent	1		
	2p <sub>3/2</sub>	2p <sub>1/2</sub>	2p <sub>3/2</sub>	2p <sub>1/2</sub>			
	FWHM = 1.4		FWHM = 0.9		FWHM = 2.5	FWHM = 2.6	FWHM = 1.6
2.3Cu/Mg-Al	932.1	951.9	932.2	952.0	50.8	74.6	529.8, 531.3
	FWHM = 1.5		FWHM = 0.9		FWHM = 2.5	FWHM = 2.7	FWHM = 1.7
4.8Cu/Mg-Al	932.2	952.0	932.2	952.0	51.0	74.7	530.3, 531.4
	FWHM = 1.6		FWHM = 1.3		FWHM = 2.4	FWHM = 2.7	FWHM = 1.8
7.3Cu/Mg-Al	932.3	952.1	932.3	952.1	51.1	74.7	530.3, 531.1
	FWHM = 1.6		FWHM = 1.2		FWHM = 2.5	FWHM = 2.8	FWHM = 1.8
9.6Cu/Mg-Al	932.3	952.1	932.3	952.1	51.2	74.8	530.3, 531.0

### Catalytic activity for CO<sub>2</sub> hydrogenation to methanol

We tested the reaction over all the prepared catalysts (4.8Cu/Al, 4.8Cu/Mg, 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al) at the same reaction conditions, where the temperature was between 200-280 °C, Pressure =30 bar, WHSV = 7200 ml  $g_{cat}^{-1}$  h<sup>-1</sup> and Feed composition of CO<sub>2</sub>: H<sub>2</sub>: N<sub>2</sub> = 1:3:1. The CO<sub>2</sub> conversion, methanol selectivity, CO selectivity, and methanol formation rate are presented in Figure 5 (A), 5 (B), 5 (C), and 5 (D), respectively. Methanol, carbon monoxide, and water were the major products detected during the reaction. We have explored the individual role of the MgO and y-Al<sub>2</sub>O<sub>3</sub> also studied and their catalytic activity in the hydrogenation reaction. In addition of Cu/Mg-Al catalysts, we have also performed the catalytic activity of Cu/MgO and Cu/γ-Al<sub>2</sub>O<sub>3</sub>. The MgO-free binary Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst showed low activity, similarly γ-Al<sub>2</sub>O<sub>3</sub>free binary Cu/MgO catalyst also showed low activity. We believe that dispersion of Cu increases over MgO-y-Al<sub>2</sub>O<sub>3</sub> when Cu loading was less than 5 wt% and it form small Cu particles at the same time synergetic effect between small Cu-particles and The 2.3Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts showed 5.4%, 6.2% and 5.2% conversion of  $CO_2$  with 95.6%, 93.4% and 90.3% of selectivity of methanol at 200 °C and 12.5%,12.7% and 11.6% of CO<sub>2</sub> conversion with 53.6%, 55.7% and 53.8% selectivity of methanol, respectively at 280 °C. The required activation energy for CO2 activation over the active particles reached at 200 °C, and the maximum CH<sub>3</sub>OH yield was achieved at 260 °C. Further increase in temperature resulted in the drop of methanol selectivity and yield. The continuous decrease in CH<sub>3</sub>OH selectivity is due to the fact that with increasing temperature, the RWGS reaction became dominant over methanol formation. Figure 5C shows CO selectivity during CO2 hydrogenation reaction over 4.8Cu/Mg-Al catalyst. The 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalyst showed very low CO2 conversion and methanol selectivity during the catalysis. This reason may be due to the uncontrolled deposition of Cu resulted in larger sized Cu-species 44, 56 with a very less number of smaller active Cu-species present in the catalyst.

## 5

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**Figure 5.** (A) CO<sub>2</sub> conversion, (B) Methanol selectivity, (C) CO selectivity, and (D) Methanol formation rate from CO<sub>2</sub> hydrogenation over a different of catalysts. Reaction condition: Temperature (200-280 °C), Pressure (30 bar), WHSV (7200 ml  $g_{cat}$ <sup>-1</sup> h<sup>-1</sup>) and Feed ratio (CO<sub>2</sub>: H<sub>2</sub>: N<sub>2</sub> = 1:3:1).

Cu is an active metal for promoting methanol synthesis via CO<sub>2</sub> hydrogenation, where the size of the copper particle plays an important role, which affects the activity of the catalyst 57, 58. As the size of the active Cu species increases, the reducibility of the catalyst decreases, affecting the activity of the catalyst 59-63. It was observed that small Cu particle size and the nature of the support plays an important role in increasing the activity of the catalyst 64-66. For 4.8Cu/Mg-Al catalyst, TEM images show that the Cu particle size is about 5-8 nm, which was further confirmed by the metal dispersion analysis via the N2O titration method, where the Cu particle size is 5.5 nm. The difference in the active species particle sizes can be explained by the fact that in TEM images, only a portion of the catalyst is analyzed, and very small Cu-particles were not detected by the technique. On the other hand, during metal dispersion analysis, very small Cu-species particles were also contributed to H<sub>2</sub> chemisorption 67. The high activity of 4.8Cu/Mg-Al catalyst is due to the presence of very small Cu-particles, which lowered the activation energy of CO2. It was observed that with increasing Cu loading, the Cu particle size increases, and metal dispersion is decreasing. The rate of methanol formation of all synthesized catalysts against different temperatures is shown in Figure 5D. The 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al and 9.6Cu/Mg-Al catalysts showed methanol formation rate of 0.012, 0.016 and 0.011 and 0.010 mol  $g_{Cu}^{-1}$  h<sup>-1</sup>, respectively at 200 °C and 0.012, 0.016, 0.013 and 0.011 mol  $g_{Cu}^{-1}$  h<sup>-1</sup>, respectively at 280 °C.

It was found that the activity in terms of the methanol formation rate of the different catalysts is directly correlated with the Cu surface area, and Cu particle size, as shown in Figure 6A. It is clear that the Cu surface area and activity are strongly associated where catalysts with large copper surface areas show a high methanol production rate. It was found that the Cu surface area increases expectedly with increasing metal dispersion because the dispersion of metal is opposite to the radius of a spherical particle <sup>68</sup>. Figure 6A, the 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts exhibited 19.4, 18.7, 14.8, and 11.8% metal dispersion with the 21.6, 20.8, 17.1, and 14.2 m<sup>2</sup>g<sup>-1</sup> Cu surface area, respectively (Table 2).

2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts also showing a similar trend and methanol formation rate of 0.012, 0.016, 0.011 and 0.010 mol g<sub>Cu</sub><sup>-1</sup> h<sup>-1</sup>, respectively at the optimum temperature (200 °C). So, it can be seen that the 4.8Cu/Mg-Al catalyst exhibited the best performing with high methanol production rate, which has the maximum copper dispersion with the highest copper surface area. On the contrary, it was also observed that the methanol formation rate is increasing with increasing temperature for all the prepared catalysts. Most investigators have observed a similar linear relationship between copper surface area and catalytic activity 69-73. The presence of the active copper atom affects the methanol formation rate, which was calculated from the Cu particle size for the various catalysts, shown in Figure 6B, where a high methanol formation rate was achieved with smaller Cu particles. The 2.3Cu/Mg-Al, 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts showed the methanol production rates of 0.012, 0.016, 0.011 and 0.010 mol  $q_{Cu}^{-1}$  h<sup>-1</sup>, and the Cu particles size was 5.3, 5.5, 6.8, 8.7, respectively. Although a direct linear correlation between the methanol formation rates and catalyst Cu surface area or Cu particle size was not found, a good linear correlation was observed for the methanol formation rate vs number of active site Cu as shown in Figure S6 (supporting information). In addition, for the 4.8Cu/Mg-Al, 7.3Cu/Mg-Al, and 9.6Cu/Mg-Al catalysts the catalyst activity (rate of methanol formation) was found to be in good correlation the 2.3Cu/Mg-Al catalyst was found to be an outlier. It was because although the 2.3Cu/Mg-Al catalyst have a higher surface area (21.6 m<sup>2</sup>g<sup>-1</sup>) ompared to 4.8Cu/Mg-Al catalyst (20.8 m<sup>2</sup>g<sup>-1</sup>), the number of active Cu particles were found to be almost same (2.97 x 1015 atom/g for 2.3Cu/Mg-Al and 5.90 x 10<sup>15</sup> atom/g for 4.8Cu/Mg-Al).



Figure 6. (A) Methanol formation rate vs. copper surface area, and (B) Methanol formation rate vs. Cu particle size.

To examine the long-term stability of the most efficient 4.8Cu/Mg-Al catalyst under optimized reaction conditions,  $CO_2$  hydrogenation to the desired product methanol was carried out for 100 h time stream, during which the reactor was operated continuously under test conditions. Figure S7 indicates both conversion of  $CO_2$  and selectivity of methanol at 200 °C for 100 h. The  $CO_2$  conversion and methanol selectivity of the 4.8Cu/Mg-Al catalyst was unchanged after 100 h reaction, confirming the very high stability of the catalyst. It was clear that methanol production and  $CO_2$  conversion is quite high over 4.8Cu/Mg-Al catalyst. The TEM images in Figure 2b shows no change of copper particles size of 4.8Cu/Mg-Al during catalysis.

#### DFT calculation for hydrogenation of CO<sub>2</sub> to methanol

The geometry optimized structures of the MgO (100) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface slabs were shown in Figure 7. The oxygen terminated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface was found to be more stable compared to the AI terminated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface. CO<sub>2</sub> molecule binds weakly to both the MgO (100) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surfaces, -49.4 kJ/mol, and -35.5 kJ/mol, respectively (Figure 7). Preferable adsorption at the MgO (100) surface indicates higher basicity of the MgO support. The CO<sub>2</sub> TPD spectra, shown in Figure 3B, also show similar trends as observed from DFT.



Figure 7. Adsorption geometry of CO<sub>2</sub> over the (a) MgO (100) and (b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surfaces. Color code: Mg (green), Al (pink), O (red) and C (black).

To understand the high metal dispersion and high stability against agglomeration at high temperatures, the adsorption of Cu atom and three small Cu clusters (Cu<sub>1</sub>, Cu<sub>4</sub> and Cu<sub>13</sub>) were studied over the MgO (100) and y-Al<sub>2</sub>O<sub>3</sub> (100) surfaces. DFT optimized geometry of Cu, Cu<sub>4</sub>, and Cu<sub>13</sub> clusters adsorbed on the MgO (100) surface is shown in Figure 8. The single Cu atom binds to the surface oxygen atom of MgO (100) at the on-top position, as shown in Figure 8(a). The Cu-O bond in the Cu/MgO (100) was calculated to be 2.17Å. The Cu<sub>4</sub> nanocluster also binds to the MgO (100) surface in a similar configuration forming two Cu-O bonds (2.17Å and 2.0Å), as shown in Figure 8(b). The bigger Cu<sub>13</sub> cluster forms multiple Cu-O bonds with the MgO(100) surface, as shown in Figure 8(c). The geometry of Cu<sub>13</sub> nanocluster remained intact upon adsorption at the MgO (100) surface. The Cu-O bonds in the Cu<sub>13</sub>/MgO (100) were calculated to be (2.11Å, 2.12Å, 2.12Å, and 2.19Å), as shown in Figure 8(c).



Figure 8. DFT optimized geometry of Cu,  $Cu_4$ , and  $Cu_{13}$  nanoclusters adsorbed at the MgO (100) surface. Color code: Mg (green), O (red), and Cu (marron).

Similarly, the adsorption of Cu atom and Cu nanoclusters were studied over the  $\gamma\text{-Al}_2O_3$  (100) surface, as shown in Figure 9.

The single Cu atom binds to both the surface oxygen and Al atoms of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100), as shown in Figure 9(a). The Cu-O bond in the Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) was calculated to be 2.06Å, whereas the Cu-Al bond length was calculated to be 2.60Å (Figure 9(a)). The Cu<sub>4</sub> nanocluster also binds to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) surface forming two Cu-O bonds (2.07Å and 2.01Å) and one Cu-Al bond (2.53 Å), as shown in Figure 9(b). The bigger Cu<sub>13</sub> cluster form multiple Cu-O bonds with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface, as shown in Figure 9(c). The four Cu-O bonds in the Cu<sub>13</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) were calculated to be 2.23Å, 2.13Å, 2.11Å, and 2.10Å, and the Cu-Al bond calculated 2.55 Å, as shown in Figure 9(c).



Figure 9. DFT optimized geometry of Cu, Cu<sub>4</sub> and Cu<sub>13</sub> nanoclusters adsorbed at the  $\gamma$ -Al\_2O\_3 (100) surface. Color code: Al(pink), O (red) and Cu (marron).

The Cu single atom and both the Cu<sub>4</sub> and Cu<sub>13</sub> nanoclusters bind very strongly to the MgO (100) surface, as can be observed from the high adsorption energy, shown in Figure 10A. The adsorption energy of Cu, Cu<sub>4</sub>, and Cu<sub>13</sub> clusters were calculated to be -71.7 kJ/mol, -201.9 kJ/mol, and -179.7 kJ/mol, respectively (Figure 10A). The Cu<sub>4</sub> nanocluster binds comparatively stronger compared to a single Cu atom and a bigger Cu<sub>13</sub> cluster. The weaker adsorption energy of Cu<sub>13</sub> nanocluster can be attributed to the high stability of Cu<sub>13</sub> cluster in gas-phase due to the presence of magic number Cu atoms. However, the adsorption energy per atom was found to decrease monotonically as the cluster size increases Cu (-71.7 kJ/mol) > Cu<sub>4</sub> (-50.5 kJ/mol) > Cu<sub>13</sub> (-13.8 kJ/mol) (Figure 10A). Due to the strong metal-support interaction in the Cu/MgO catalyst, the small catalyst nanoparticle will be stable against agglomeration, as observed experimentally.



**Figure 10.** (A) Adsorption energy of Cu, Cu<sub>4</sub>, and Cu<sub>13</sub> nanoclusters adsorbed at the MgO (100) surface and (B) Adsorption energy of Cu, Cu<sub>4</sub>, and Cu<sub>13</sub> nanoclusters adsorbed at the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface.

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Similar to the MgO (100) surface, the Cu single atom and both the Cu<sub>4</sub> and Cu<sub>13</sub> nanoclusters bind very strongly to the y-Al<sub>2</sub>O<sub>3</sub> (100) surface, as shown in Figure 10B. The adsorption energy of Cu and Cu<sub>4</sub> clusters were calculated to be -91.6 kJ/mol and -229.1 kJ/mol, respectively (Figure 10B), which are comparatively higher compared to the adsorption energy values obtained over the MgO (100) surface. The corrugated nature of the y-Al<sub>2</sub>O<sub>3</sub> (100) surface may be the reason for the high adsorption of the small Cu cluster. However, the bigger Cu<sub>13</sub> cluster adsorbed weaker (-168.5 kJ/mol) at the y-Al<sub>2</sub>O<sub>3</sub> (100) surface compared to the Cu<sub>13</sub> cluster adsorption at the MgO (100) surface (-179.7 kJ/mol). Similar to the trends observed over the MgO (100) surface, over the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface the Cu<sub>4</sub> nanocluster binds comparatively stronger compared to single Cu atom and bigger Cu<sub>13</sub> clusters. Similarly, the adsorption energy per atom was found to decrease monotonically as the cluster size increases Cu (-91.6 kJ/mol) > Cu<sub>4</sub> (-57.3 kJ/mol) > Cu<sub>13</sub> (-13.0 kJ/mol) (Figure 10B). The higher adsorption energy of the Cu<sub>13</sub> cluster at the MgO (100) compared to the y-Al<sub>2</sub>O<sub>3</sub> (100) surface is due to the higher basicity of the MgO system compared to y-Al<sub>2</sub>O<sub>3</sub>. Due to higher basicity, the electron transfer from the MgO to the Cu<sub>13</sub> cluster is higher compared to Lewis acidic y-Al<sub>2</sub>O<sub>3</sub> surface, which makes the  $Cu-O_{(support)}$  interaction much stronger. Though the agglomeration of the Cu clusters is thermodynamically still favorable over MgO/y-Al<sub>2</sub>O<sub>3</sub> support, due to the strong metal-support interaction in the Cu/MgO/y-Al<sub>2</sub>O<sub>3</sub> catalyst will be less energetically favorable compared to the gasphase agglomeration, as shown in Figure S10. Similar observation was made by Wang et al. for growth of Cu particle on γ-Al<sub>2</sub>O<sub>3</sub> surface <sup>74</sup>. The strong metal-support interaction in the Cu/MgO/y-Al2O3 catalyst also stabilizes the small catalyst nanoparticle against diffusion at the catalyst surface also may reduce the tendency for forming agglomerate, as observed experimentally.

To understand the activity and selectivity trends of the Cu/MgO/ y-Al<sub>2</sub>O<sub>3</sub> catalyst, DFT method was used to calculate the formation energies of surface adsorbed intermediate CO2\*, COOH\*, HCOO\* and H\* at the Cu<sub>13</sub>/MgO (100) and Cu<sub>13</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (100) metal/support interface, as shown in Figure 11 and Figure 12. The adsorption of the CO2 molecule at the Cu13/MgO active site (-120.9 kJ/mol) is found to be preferable by ~ 57 kJ/mol compared to the  $Cu_{13}/\gamma\text{-}Al_2O_3$  (100) active site (-64.2 kJ/mol). The basic nature of the MgO support enhances the adsorption of CO2 molecules evident from the above observation. The CO2 molecule bind to the  $Cu_{13}/MgO$  (100) interface by forming bonds with both the Cu<sub>13</sub> nanoparticle as well as the MgO support, as shown in Figure 11 (a). The C-Cu(1), C-Cu(2), O-Mg and O-Cu bond distances were calculated as 2.05Å, 2.39Å, 2.12Å and 2.08 Å, respectively, (Figure 11(a)). This is not the case for the  $CO_2$  adsorption at the  $Cu_{13}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) active site, where the CO<sub>2</sub> only formed a bond with the Cu<sub>13</sub> metal cluster (Figure 12(a)). The C-Cu and O-Cu bond distances were calculated as 2.11Å and 2.07Å, respectively (Figure 12(a)). Similar trends were also observed for the adsorption energy of the H atom, which preferentially binds to the Cu<sub>13</sub>/MgO (100) active site (-130.4 kJ/mol) compared to the Cu<sub>13</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (100) active site (-85.7 kJ/mol). The favourable adsorption energy trends for the CO2 and H at the Cu13/MgO (100) interface indicate Cu/MgO (100) to be the prominent active site for this reaction. Formation of methanol from the hydrogenation of CO<sub>2</sub> mainly commence through two distinct intermediates, the carboxylate (COOH\*) and formate (HCOO\*) surface intermediates. The adsorption geometry of the COOH\* and HCOO\* intermediates were shown in Figure 11(b) and 14(c). Similar to CO<sub>2</sub> adsorption, Both the COOH\* and HCOO\* intermediates bind preferably to the Cu<sub>13</sub>/MgO (100) interface forming bond with both the Cu<sub>13</sub> nanocluster and MgO (100) surface. The C-Cu and O-Mg bond distances for the COOH\* adsorption (Figure 11(b) were calculated as 1.99Å and 2.21Å. Whereas for the HCOO\* adsorption the C-Cu, O-Mg and O-Cu bond distances (Figure 11(c) were measured to be 2.13Å, 2.19Å and 2.04Å, respectively. The high selectivity observed in this reaction possibly indicate that the formate pathway is preferable here. The main side product CO can be formed from the CO-OH bond dissociation of COOH intermediate, whereas the formate pathway is not known to produce CO. As can be observed in the formation energy values given in Table 4, the formation HCOO\* surface intermediate (-257.2 kJ/mol) is more favorbale compared to the COOH\* intermediate (-131 kJ/mol) by nearly -126 kJ/mol at the Cu13/MgO (100) active site. Similar observations also made for the Cu<sub>13</sub>/y-Al<sub>2</sub>O<sub>3</sub> (100) active site, however, the adsorption energies of both the HCOO\* and COOH\* intermediate were much weaker compared to the Cu/MgO (100) site. The preferable formation of the HCOO\* intermediate over the COOH\* intermediate at the Cu/MgO (100) active site may be the reason for the high methanol selectivity seen of the Cu/MgO/y-Al<sub>2</sub>O<sub>3</sub> catalyst.

Table 4. Adsorption energies ( $E_{ads}$ ) of surface intermediates CO<sub>2</sub>, H, COOH, HCOO at the Cu<sub>13</sub>/MgO (100), and Cu<sub>13</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) catalyst interface. The gas-phase CO<sub>2</sub> and H<sub>2</sub> were used as a reference.

E	E <sub>ads</sub> (kJ/mol)	Cu <sub>13/</sub> MgO (100)	Cu <sub>13</sub> /γ-Al <sub>2</sub> O <sub>3</sub> (100)
	CO <sub>2</sub> *	-120.9	-64.2
	H*	-130.4	-85.7
	COOH*	-131.0	-89.9
	HCOO*	-257.2	-197.8

In this study, we have used energies of  $CO_2(g)$  and  $H_2(g)$  as reference gas-phase energies to calculate the adsorption energies of HCOO\* and COOH\*, as given in equation 3 in DFT Method (supporting information). Previous studies by Liu et al. 75, Marvikakis et al. <sup>76</sup>, Liu et al. <sup>77</sup>, the authors have used the gasphase energies of the intermediate species HCOO(g) and COOH(g) for the calculation of the adsorption energies of their respective adsorbed species. To compare with the literature, we have calculated the adsorption energies of H\*, COOH\* and HCOO\* relative to their gas-phase species. The adsorption energies obtained in this study (given in the Table S4) are comparable to the adsorption values obtained by Liu et al. <sup>75</sup> at the Custrip-ZrO2 interface. The adsorption energies obtained for the adsorbate species CO2\*, H\*, COOH\* and HCOO\* over the Cu<sub>13</sub>/MgO (100) are higher compared to the values obtained by Liu et al. <sup>75</sup> at the Cu<sub>strip</sub>/ZrO<sub>2</sub> interface, as can be seen in the table S4. At the  $Cu_{13}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface, the CO<sub>2</sub> adsorption energy was found to be comparable to the value obtained by Liu et al. 75, whereas the adsorption energies for COOH\* was weaker by 30 kJ/mol at the  $Cu_{13}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface. The adsorption energies of H\* and HCOO\* were calculated to be higher at the  $Cu_{13}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) surface compared to the Cu<sub>strip</sub>/ZrO<sub>2</sub> interface studied by Liu et al. <sup>75</sup> as given in Table S5 (supporting information). The co-adsorption of H with surface

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adsorbate CO<sub>2</sub>, COOH and HCOO were studied as shown in Figure S8 (supporting information). The adsorption energy of coadsorbed H+CO<sub>2</sub> was calculated to be -135.8 kJ/mol (Table S5), which is much smaller compared to the sum of the adsorption energy of H (-130.4 kJ/mol, Table 4) and CO<sub>2</sub> (-120.9 kJ/mol, Table 4). Similarly, the adsorption energy of co-adsorbed H+COOH (-117.3 kJ/mol, Table S5) and H+HCOO (-235.9 kJ/mol, Table S5) were also calculated to be smaller compared to the sum of the individual species adsorption energies. The weaker adsorption energies calculated for the co-adsorbed state can be attributed to the adsorbate-adsorbate interaction and crowding of the adsorbate in the small Cu<sub>13</sub> metal cluster <sup>78-81</sup>.



Figure 11. Adsorption geometry of CO<sub>2</sub>, COOH, HCOO, and H surface intermediates at the Cu<sub>13</sub>/MgO (100) active site. Color code: Mg (green), O (red), C (black), H (white) and Cu (marron).



Figure 12. Adsorption geometry of CO<sub>2</sub>, COOH, HCOO and H surface intermediates at the Cu<sub>13</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100) active site. Color code: AI (pink), O (red), C (black), H (white) and Cu (marron).

To understand the effect of Cu nanocluster size, additional DFT calculation were done to obtain the adsorption energies of CO<sub>2</sub>, COOH, HCOO and H surface intermediates over the Cu<sub>1</sub>/MgO(100) and Cu<sub>4</sub>/MgO(100) active site. The DFT obtained geometry optimized structures of CO<sub>2</sub>, COOH, HCOO and H adsorbed at the Cu<sub>1</sub>/MgO(100) and Cu<sub>4</sub>/MgO(100) surface shown in Figure 13.



Figure 13. Adsorption geometry of  $CO_2$ , COOH, HCOO, and H surface intermediates at the (a-d)  $Cu_1/MgO(100)$  and (e-f)  $Cu_4/MgO(100)$  active sites. Color code: Mg (green), O (red), C (black), H (white) and Cu (marron).

The CO<sub>2</sub> molecule adsorbs at the Cu<sub>1</sub>/MgO (100) active site (-51.4 kJ/mol, Table 5) forming bond with both the metal Cu and Mg of MgO support, as shown in Figure 13 (a). The C-Cu and O-Mg bond distances were calculated as 2.00Å, and 2.26Å, respectively (Figure 13(a)). Similar binding configuration was also observed at the Cu<sub>4</sub>/MgO (100) active site, where the CO<sub>2</sub> formed two Cu-C bonds and a Mg-O bond (Figure 13(e)). The C-Cu<sup>(1)</sup>, C-Cu<sup>(2)</sup> and O-Cu bond distances were calculated as 2.02Å, 2.17 Å and 2.24Å, respectively (Figure 13(e)). The binding energy of CO2 at the Cu4/MgO (100) active site was calculated to be -72.4 kJ/mol (Table 5), which is ~ 20 kJ/mol stronger compared to Cu1/MgO (100) active site, but ~ 50 kJ/mol weaker compared to Cu<sub>13</sub>/MgO (100) active site. The adsorption energy of  $CO_2$  increases following the trend:  $Cu_1/MgO$  (100) <  $Cu_4/MgO$  (100) <  $Cu_{13}/MgO$  (100). The adsorption of H at the Cu<sub>1</sub>/MgO (100) active site was found to be on-top of the Cu atom (Cu-H bond distance 1.50 Å), as shown in Figure 13(d), The adsorption geometry of H was found to be bridging in Cu<sub>4</sub>/MgO (100) active site, forming two Cu-H bonds (1.69Å and 1.64Å), as shown in Figure 13(h). The adsorption energy of H at the Cu<sub>1</sub>/MgO (100) and Cu<sub>4</sub>/MgO (100) active sites were calculated to be -117.5 kJ/mol and 8.2 kJ/mol, respectively (Table 5). The hydrogenation of adsorbed CO<sub>2</sub> will give two important surface intermediates COOH\* and HCOO\*. The DFT optimized geometries of COOH\* and HCOO\* intermediates at the Cu<sub>1</sub>/MgO (100) active site were shown in Figure 13(b) and 14(c), respectively. The COOH\* intermediate bind only to the Cu atom at the Cu<sub>1</sub>/MgO (100) interface (Cu-C bond length 1.89Å), whereas the HCOO\* intermediate bind to both the Cu atom and MgO (100) surface, as shown in Figure 13(c), forming C-Cu and O-Mg bonds (1.91Å and 2.22Å, respectively). As can be observed in the formation energy values given in Table 5, the formation HCOO\* surface intermediate (-221.5 kJ/mol, Table 5) is more favorbale compared to the COOH\* intermediate (-143.8 kJ/mol, Table 5) by nearly -77 kJ/mol at the Cu<sub>1</sub>/MgO (100) active site. Similar observations also made for the Cu<sub>4</sub>/MgO (100) active site, where the formation HCOO\* surface intermediate (-114.1 kJ/mol, Table 5) is more favorbale compared to the COOH\* intermediate (-6.7 kJ/mol, Table 5) by nearly -107 kJ/mol, however the adsorption energies of both the HCOO\* and COOH\* intermedia were much weaker compared to the Cu<sub>1</sub>/MgO (100) site. The COOH\* and HCOO\* intermediates bind both to the Cu atom and the MgO support as shown in Figure 13(f) and 14(g), respectively. The C-Cu and O-Mg bonds for the COOH\* intermediate at the Cu<sub>4</sub>/MgO (100) interface was measured to be 1.96Å and 2.15Å (Figure 13(f)). The HCOO\* intermediate bind to the Cu4 cluster forming two O-Cu bonds (2.15Å and 2.01Å) and also bind the MgO support forming O-Mg bond (2.31Å), as shown in Figure 13(g). The preferable formation of the HCOO\* intermediate over the COOH\* intermediate at the all the three surfaces with different Cu cluster Cu<sub>1</sub>/MgO (100), Cu<sub>4</sub>/MgO (100) and Cu<sub>13</sub>/MgO (100) active sites further indicate to the high methanol selectivity seen of the Cu/MgO/γ-Al<sub>2</sub>O<sub>3</sub> catalyst.

**Table 5.** Adsorption energies ( $E_{ads}$ ) of surface intermediates CO<sub>2</sub>, H, COOH, HCOO at the Cu<sub>1</sub>/MgO (100), and Cu<sub>4</sub>/MgO (100) catalyst interface. The gasphase CO<sub>2</sub> and H<sub>2</sub> were used as the reference state.

E <sub>ads</sub> (kJ/mol)	Cu₁/MgO (100)	Cu₄/MgO (100)	
CO <sub>2</sub> *	-51.5	-72.4	
H*	-117.5	8.2	
COOH*	-143.9	-6.71	
HCOO*	-221.5	-114.1	

Previous studies have in general shown the CO<sub>2</sub> hydrogenation barrier to be smaller for HCOO formation in comparison to COOH formation. Huš et al.82 calculated the activation barrier for  $CO_2^*+H^* \rightarrow HCOO^*$  over four different catalyst surfaces Zn<sub>3</sub>O<sub>3</sub>/Cu, Mg<sub>3</sub>O<sub>3</sub>/Cu, Cr<sub>3</sub>O<sub>3</sub>/Cu and Fe<sub>3</sub>O<sub>3</sub>/Cu to be 56.9 kJ/mol, 45.4 kJ/mol, 68.5 kJ/mol and 11.6 kJ/mol which were smaller compared to the  $CO_2^*+H^* \rightarrow COOH^*$ , which were 68.5 kJ/mol, 73.3 kJ/mol, 84.9 kJ/mol and 61.8 kJ/mol. Similarly, Zhang et al.<sup>83</sup> calculated the activation barrier for CO<sub>2</sub> hydrogenation to HCOO to be 93.1 kJ/mol over Cu<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> surface, whereas the activation barrier for COOH formation calculated to be higher (212.2 kJ/mol). Similar activation energies were also observed by Grabow et al.<sup>76</sup> over Cu(111) surface where the HCOO\* formation activation barrier (84.0 kJ/mol) was found to be smaller compared to COOH\* formation activation barrier 171.8 kJ/mol. Frei et al.84 also found the COOH\* formation to have a higher barrier compared to the HCOO\* formation.

## Conclusion

Nanocrystalline Cu/Mg-Al oxide catalysts were prepared by the sol-gel method, where ~ 5wt% Cu was the optimum loading showing the formation of copper nanoparticles with size ~ 5 nm with high Cu surface area, and dispersion, which directly influence the catalytic performances. Smaller particles consist of significantly more active Cu species, showing very high Cu dispersion favouring higher adsorption of  $CO_2$ , giving > 99% methanol selectivity. H<sub>2</sub>-TPR shows that the metal support interaction is present for 5 wt% Cu supported Mg-Al catalyst, which favours the stability of active Cu particles against sintering. 5 wt% Cu supported Mg-Al catalyst with a methanol formation rate of 0.016 mol/gCu /h. DFT studies also revealed that strong metal-support interactions in Cu/MgO/y-Al<sub>2</sub>O<sub>3</sub> catalysts would stabilize small catalytic nanoparticles against agglomeration. The catalyst was very stable and did not show any deactivation even after 100 h time on stream. In Addition, DFT studies also revealed that the weaker adsorption energy (-179.7 kJ/mol) of Cu<sub>13</sub> nanocluster could be attributed to the high stability of Cu13 cluster in gas-phase due to the presence of magic number Cu atoms. The nanostructure catalyst will be stable against agglomeration due to the strong metal-support interaction in the Cu/MgO/y-Al<sub>2</sub>O<sub>3</sub> catalyst. As shown in the DFT study, in addition to the increase in CO<sub>2</sub> adsorption capacity, MgO was found to play the key role in the highly selective production of methanol. DFT calculation showed that the Cu/MgO (100) catalyst system highly favors the HCOO\* route compared to the COOH\* route. On the Cu<sub>13</sub>/MgO (100) surface, the HCOO\* intermediate was found to be nearly 130 kJ/mol more stable compared to the COOH\* intermediate. The difference is only ~ 110 kJ/mol on the  $Cu_{13}/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) surface. Due to the highly favorable formate (HCOO\*) route compared to the carboxylate (COOH\*) route, high selectivity for methanol was observed when MgO was added to the  $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$  catalytic system.

## **Experimental Section**

## Catalysis synthesis

Details of materials and methods used in the catalysts synthesis and, catalyst characterization details are presented in the supporting information.

## Hydrogenation of CO2 to methanol

The activity measurement of CO<sub>2</sub> hydrogenation to methanol over Cu/Mg-Al catalyst was conducted in a continuous fixed-bed tubular reactor (Figure 14). 0.5 g of the catalyst was loaded into the reactor, and a K-type thermocouple was inserted at the centre of the furnace. Before each reaction, the catalyst was initially treated (heating rate 2 °C/min) under a flow of 10 ml/min H<sub>2</sub> (10% H<sub>2</sub> in Helium) at 250 °C for 2 h under atmospheric pressure. The reactor was allowed to cool down to 190 °C, and a gas mixture of  $CO_2/H_2/N_2 = 1: 3: 1$  (flow rate:60 ml/min) was passed over the catalyst bed in the reactor to reach the reactor pressure of 3.0 MPa. The corresponding weight hourly space velocity (WHSV) was 7200 ml. g<sub>Cat</sub>-1. h-1, and the flow of gaseous mixture was passed over the catalyst bed for 18 hours at 200 °C. During this time, steady-state of the reaction was reached. Subsequently, the products were quantitatively analyzed by using online gas chromatography (Agilent 7890A), equipped with a 0 0er98765.two-column system connected to a thermal conductivity detector (TCD) using porapack-Q column (for analyzing H\_2, N\_2, CO, CO\_2, and H\_2O), and HP-Plot Q (for analyzing CH<sub>3</sub>OH and CH<sub>4</sub>). In all the experiments, CH4 concentration in the outlet gas mixture was found to be nil. Carbon balance was estimated from the conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH, CH<sub>4</sub>, and CO using N<sub>2</sub> as the internal standard. The material balance and carbon balance were calculated with an accuracy of  $\pm$  3% (between 97% and 103%). The CO<sub>2</sub> conversion ( $X_{CO2}$ ), selectivity for methanol ( $S_{CH3OH}$ ) were calculated according to the following equations:





Figure 14. Schematic diagram of continuous fixed bed reactor set-up for  $\mbox{CO}_2$  hydrogenation to methanol production.

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#### DFT calculation

Details DFT calculation of the catalysts are presented in the supporting information.

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Keywords: CO2 hydrogenation • Methanol • Sol-gel method • Cu-nanoparticles • DFT-study

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11

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## **Table of Contents**



Copper nanoparticles size supported on Mg-Al supported catalyst for  $CO_2$  hydrogenation to methanol with high methanol production rate with the range at 200-280 °C temperature.





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