

# Insights into Precursor Chemistry and Efficiency of Cu/MgO Catalysts for CO<sub>2</sub>

## Hydrogenation to Methanol

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### Highlights

- Synthesis of (Cu<sub>1-x</sub>Mg<sub>x</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (x = 0.0-0.5) precursors via hydrothermal route for the first time.
- Mg<sup>2+</sup> incorporation was increased thereby increasing catalyst efficiency of Cu/MgO towards CO<sub>2</sub> hydrogenation to methanol.
- The first-principles calculations were experimentally validated for (Cu<sub>1-x</sub>Mg<sub>x</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (x = 0.0-0.5) precursors.
- Catalyst efficiency was compared with conventionally prepared Cu/MgO catalyst.

### 1. Introduction

Methanol today is not only the most important feedstock for chemicals and fuel components but also is an important chemical and a potential energy carrier in the future. Since the early 1960s hitherto, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> ternary catalysts developed by Imperial Chemical Industries have been used commercially for methanol synthesis derived from the malachite rosasite synthesized precursors [1]. In recent years Mg<sup>2+</sup> which is an interesting replacement for Zn<sup>2+</sup>, not only because of the close match in the ionic radii, charge but also of the similarity in precursor formation chemistry with Cu<sup>2+</sup>. Moreover, it promotes the number of CO<sub>2</sub> and H<sub>2</sub> adsorption active sites and increased the metal-support interaction with high metallic Cu surface area [2]. These catalysts have been found to be structure sensitive and the activity varies depending on the conditions employed in the very first stage of catalyst synthesis i.e., precursor formation [3]. However, conventional methods of precursor synthesis suffer from interference of competing phases which ultimately lead to the activity deterioration in the final catalyst. To overcome these difficulties in the present case Cu/MgO catalyst has been synthesized using an optimized hydrothermal based precursor formation approach for the first time with an improved and efficient outcome for hydrogenation of CO<sub>2</sub> to methanol. To shed light on the structure-activity relationship, physicochemical properties and catalytic performance of catalyst obtained via hydrothermally (HT) synthesized precursor with a conventionally prepared catalyst through co-precipitation (CP) and wet impregnation (IMP) were compared. The precursor and final catalyst have been characterized with an array of instrumental techniques.

### 2. Methods

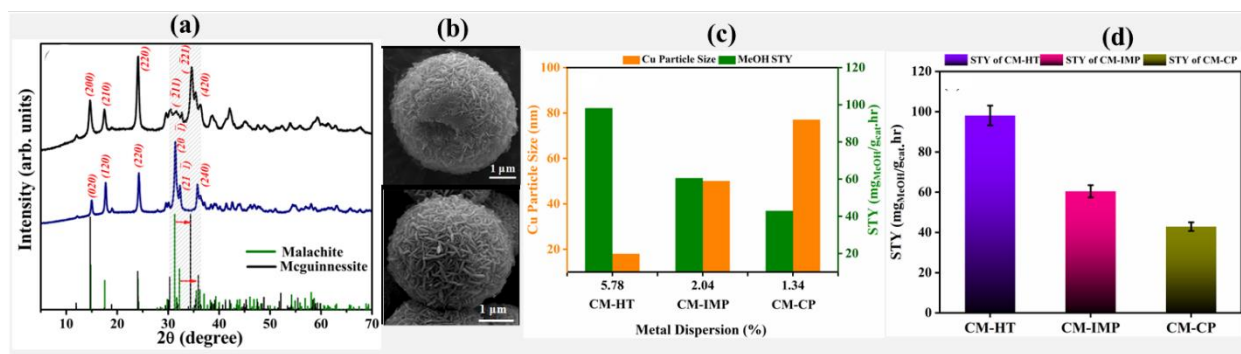
For the synthesis and optimizations of Cu-MgO catalyst, firstly the synthesis of hydroxy carbonate precursor has been carried out using a hydrothermal route using nitrate salts as reactant in the presence of carbonating agent at different set of temperature and varied durations. The pure catalyst formed were then calcined at 350 °C and 400 °C for 3 h in static air individually. The catalytic activity tests were performed in a fixed-bed reactor connected with gas chromatography for product analysis. The first principles DFT calculations of catalyst precursor were performed using the well-tested CASTEP code. The DFT calculations for Cu/MgO catalyst were performed using Dmol<sup>3</sup> program package in Material Studio (Version 2020).

### 3. Results and discussion

The calculation results obtained from the geometry optimization of a structure show that (Cu<sub>6/8</sub>Mg<sub>2/8</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> in which 25% Mg is substituted for Cu at the Cu<sub>2</sub> site is the most thermodynamically stable structure owing to its lowest formation energy (-1.863 eV) with weakest Jahn-Teller distortion. Also, the formation energies of other compositions (i.e., 1/8, 3/8, 4/8) have been compiled. The formation energy calculated for different configurations follows the stability order as (Cu<sub>6/8</sub>Mg<sub>2/8</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> > (Cu<sub>7/8</sub>Mg<sub>1/8</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> > (Cu<sub>4/8</sub>Mg<sub>4/8</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> > (Cu<sub>5/8</sub>Mg<sub>3/8</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>. Following these observations, the experiments for precursor formation were performed using the hydrothermal method and coprecipitation method. The progress of the precursor phase formation under different sets of conditions has been followed by recording the powder X-ray diffraction (PXRD) patterns. It has been found that with the right choice of carbonate source and with the right set of reaction

conditions, the desired phase can be achieved under hydrothermal treatments. Initial experiments, conducted at various temperatures of 120 °C to 180 °C for a duration of 12-20 h, evidently showed a single crystalline phase formation only at 150 °C for a duration of 16 h. The PXRD pattern of the CM50 product in comparison to CM0 obtained using  $(\text{NH}_4)_2\text{CO}_3$  as carbonate source as well as a mineralizer at 150 °C is shown in Figure 1(a). The pattern of the CM50 sample obtained showed a complete resemblance with the mcguinnessite, which is analogous to rosasite mineral crystallizing in Monoclinic symmetry (*S.G. P12<sub>1</sub>/c1*) with  $a = 12.9181 \text{ \AA}$ ;  $b = 9.3923 \text{ \AA}$ ;  $c = 3.1622 \text{ \AA}$ ,  $\beta = 111.23^\circ$  as lattice parameters. The precursor as well as catalyst obtained after calcination showed unique spongy ball like shape unlike already reported catalysts (Figure 1(b)).

The study probes into the impact of varied catalyst synthesis methods on the properties of Cu/MgO catalysts. Our findings highlight distinct physicochemical differences among CM-HT, CM-CP, and CM-IMP catalysts. Notably, CM-HT exhibited a smaller crystallite size, higher surface area, enhanced metal dispersion, and active copper surface area compared to CM-CP and CM-IMP. As a result, superior catalytic performance for  $\text{CO}_2$  hydrogenation to methanol for CM-HT was associated with improved Cu-Mg interfacial sites and enhanced metal-support interaction (Figure 1 (c) and (d)). The BET surface area,  $\text{SA}_{\text{Cu}}$ , and  $\text{D}_{\text{Cu}}$  in catalysts were found to follow the order as CM-HT ( $66.84 \text{ m}^2/\text{gm}$ ,  $20.62 \text{ m}^2/\text{gm}$ ,  $5.78 \%$ ) > CM-IMP ( $23.7 \text{ m}^2/\text{gm}$ ,  $7.01 \text{ m}^2/\text{gm}$ ,  $2.04 \%$ ) > CM-CP ( $16.46 \text{ m}^2/\text{gm}$ ,  $5.36 \text{ m}^2/\text{gm}$ ,  $1.34 \%$ ) and the MeOH STY also follow the same order CM-HT ( $98.11 \text{ mg}_{\text{MeOH}}/\text{g}_{\text{cat}}\cdot\text{hr}$ ) > CM-IMP ( $6.45 \text{ mg}_{\text{MeOH}}/\text{g}_{\text{cat}}\cdot\text{hr}$ ) > CM-CP ( $42.85 \text{ mg}_{\text{MeOH}}/\text{g}_{\text{cat}}\cdot\text{hr}$ ). The alteration in surface basicity, as evidenced by  $\text{CO}_2$ -TPD results, emphasized the pivotal role of metal-support interaction, particularly in suppressing medium basic sites ( $\beta$ ) compared to pure MgO, thereby inhibiting the rWGS reaction.



**Figure 1.** (a) PXRD pattern of Cu-Mg hydroxy carbonate precursor synthesized via hydrothermal route, (b) FESEM images of precursor and calcined catalyst, (c) Effect of copper particle size and copper metal dispersion on the catalytic performance of Cu/MgO catalysts, and (d) Overall comparison of methanol STY for Cu/MgO catalysts synthesized via different preparation methods at optimized reaction conditions.

#### 4. Conclusions

Among all the catalysts tested with the difference in preparation history, the Cu/MgO-HT catalyst demonstrates the highest catalytic activity, which resulted in a  $\text{CO}_2$  conversion of 15.17%, a methanol selectivity of 68.49%, and a methanol STY of  $98.11 \text{ mg}_{\text{MeOH}}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$  at 240 °C, 40 bar and  $\text{WHSV} = 2600 \text{ ml}/\text{g}_{\text{cat}}\cdot\text{h}$ . Moreover, this catalyst exhibits remarkable long-term stability in a 100-h run owing to the stabilization of active metal species and the inhibition of catalyst agglomeration and sintering. In conclusion, our findings highlight the potential of a new synthetic approach for efficient monophasic catalyst precursors and deepen our understanding of Cu/MgO catalysts for methanol synthesis, offering insights for future catalyst design and optimization.

#### References

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#### Keywords

“Rosasite-Mcguinnessite”, “Cu/MgO”, “ $\text{CO}_2$  hydrogenation”, “Methanol synthesis”, “Structure-activity”