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Carbon dioxide hydrogenation to value-added products using Cu-based catalytic materials

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Abstract. In this work, we report on the synthesis and evaluation of catalytic materials composed of copper/calcium oxide/alumina (Cu/CaO/Al₂O₃) for carbon dioxide conversion to value-added products. Catalytic materials were synthesized using sequential incipient wetness impregnation method. Synthesized materials with different compositions of copper and adsorbent were tested in a high-pressure packed bed reactor under a pressure $P = 60$ bars, temperature $T = 300$ °C, and hydrogen to carbon dioxide ratio ($H_2/CO_2 = 3$) to determine their performances and catalytic activities. The results of the activity revealed that CaO-based catalysts were very active in converting CO₂ to methanol and carbon monoxide. Catalyst containing 30%Cu10%CaO achieved the highest CO₂ conversion of 16.5% and a maximum methanol selectivity of 17.8%, while the lowest selectivity towards carbon monoxide (CO) were obtained using 20%Cu-containing catalyst. Reducing CaO content from 10wt% to 5wt% boosted the CO₂ conversion to 18% with higher selectivity towards CO compared to the catalyst containing 10%CaO.

1. Introduction

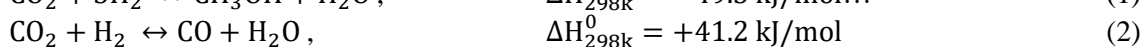
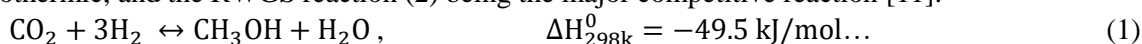
Due to the world's fast economic expansion, energy demand has increased significantly in recent decades and is anticipated to rise even more in the next years causing several global environment issues and jeopardizing future generations wellbeing and life. Indeed, fossil fuels as the dominant energy source are the main contributor for CO₂ gas emissions reported to increase at a rate of 2.4 ppm/year, projecting a negative picture of CO₂ concentration in the atmosphere [1]. It is estimated that CO₂ level will surpass a catastrophic concentration limit of 570 ppm by the end of 21st century if no proper CO₂ abatement policies are implemented or no stringent mitigations methods are taken [2]. CO₂ emissions are thought to be the main reason of the associated rising temperature of the earth's average surface that is expected to lay between 1.4 and 5.8 °C in 2100 [3]. Therefore, developing new technologies to tackle carbon emissions is crucial.

For CO₂ mitigations, a variety of techniques and treatment technologies have been employed. Carbon capture and storage (CCS) has been extensively studied. CO₂ utilization has been investigated where CO₂ emissions with high concentration can be used as a free carbon source to produce valuable hydrocarbon particularly via thermal catalysis [4], electrocatalysis [5] and photocatalysis [6]. Nonetheless, these processes have their pitfalls, including temperature swings, intensive energy requirements, and the cost of CO₂ transportation [7, 8]. Owing to the limitations associated with the strategies of transportation and storage during the CO₂ separation and compression steps, attention has shifted towards an alternative solution combining both adsorption and conversion in one integrated

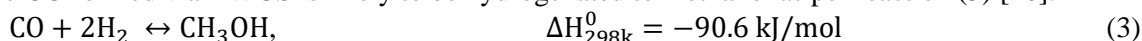


process. Therefore, coupling CO₂ capture and conversion has acquired an interest in research [9]. Development of novel catalytic materials is very crucial for the implementation of integrated carbon capture and utilization (ICCU). Targeting CO₂ hydrogenation to methanol using renewable hydrogen is a promising environmental-friendly pathway for tackling CO₂ emissions. Globally, methanol is nowadays one of the top five shipped chemicals. Methanol is a primary raw material, and valuable chemical industry that can be used as fuel or as intermediate to produce value-added products including formaldehyde, acetic acid, and biodiesel [10].

Methanol synthesis by CO₂ hydrogenation occurs through reactions (1) and (3), which are exothermic, and the RWGS reaction (2) being the major competitive reaction [11]:



The CO formed via RWGS is likely to be hydrogenated to methanol as per reaction (3) [20].



In the present work, we synthesized a novel highly active Cu-based catalysts for CO₂ hydrogenation to value added products. Copper was chosen as catalytic active component for facilitating the hydrogen adsorption and spill over, whereas, CaO was selected as an effective adsorbent taking into account the special qualities and attributes of nano CaO dispersed over Al₂O₃ support.

2. Materials and methods

2.1. Materials

Chemicals used in this work were alumina (γ -Al₂O₃ PURLOX TH100/150) obtained free of charge of SASOL, USA. Sodium carbonate (Na₂CO₃, 99% purity) was purchased from Fluka chemical, Germany. Aqueous precursor solutions of calcium nitrate tetrahydrate (Ca(NO₃)₂·3H₂O, 99%, was purchased from BDH, UK while copper nitrate tetrahydrate (Cu(NO₃)₂·6H₂O (6H₂O), 99%) was purchased from Research Lab Fine Chem industries, India. All chemicals and precursors in this study were used as received without further purification. Distilled water was used throughout the experiments.

2.2. Synthesis of the Catalysts

Alkali and alkaline metal adsorbents supported on γ -Al₂O₃ were synthesized via the sequential incipient wetness impregnation method [12]. Two different loading of adsorbent namely 5wt% CaO and 10wt% CaO, were used to modify the carrier γ -Al₂O₃. Copper (Cu) based catalysts with different compositions were synthesized. A summary of synthesised catalysts is given in Table 1. A schematic representation of the synthesis procedure is given in Figure 1.

Table 1. The abbreviation of the prepared catalysts and their corresponding compositions.

No.	Sample	Used abbreviation	Composition, weight %	
			CaO	Cu
1	10%Cu10%CaO/Al ₂ O ₃	10Cu10CaO	10	10
2	20%Cu10%CaO/Al ₂ O ₃	20Cu10CaO	10	20
3	30%Cu10%CaO/Al ₂ O ₃	30Cu10CaO	10	30
4	20%Cu5%CaO/Al ₂ O ₃	20Cu5CaO	5	20

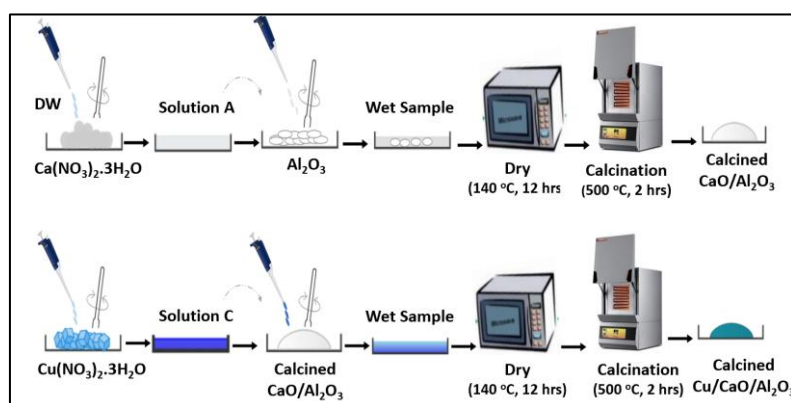


Figure 1. Synthesis procedure of catalytic materials

2.3. Activity measurements of the catalysts

Carbon dioxide hydrogenation performance over synthesized catalysts were evaluated using a high-pressure lab-scale test unit (PID, Micrometrics) dotted with a hastelloy fixed bed reactor having an internal diameter of 9.3 mm. A schematic diagram of the experimental setup is shown in Figure 2. For each run, 500 mg of powdered catalyst was loaded in the middle of the fixed bed surrounded by two layers of quartz wool. The catalyst was first reduced under pure hydrogen (H_2) flow of $20 \text{ ml}\cdot\text{min}^{-1}$ at $450 \text{ }^\circ\text{C}$ with a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ for two hours. The activated catalyst was then purged in a flow of $20 \text{ ml}\cdot\text{min}^{-1}$ of pure nitrogen (N_2) for five minutes and the reactor was cooled down to 300°C . The feed gas made of a mixture of $\text{CO}_2:H_2$ with ratio of 3:1 at a flow rate of $60 \text{ ml}\cdot\text{min}^{-1}$ was then introduced to the reactor followed by gradual increase of the total pressure to 60 bars. The gaseous and liquid products were separated in a cold trap. The gaseous products were analyzed online using a gas chromatograph equipped with thermal conductivity detector (GC-TCD), whereas the liquid products collected in a trap (5°C) were analysed offline by gas chromatography (GC Agilent 7890) equipped with a flame ionization detector (GC-FID).

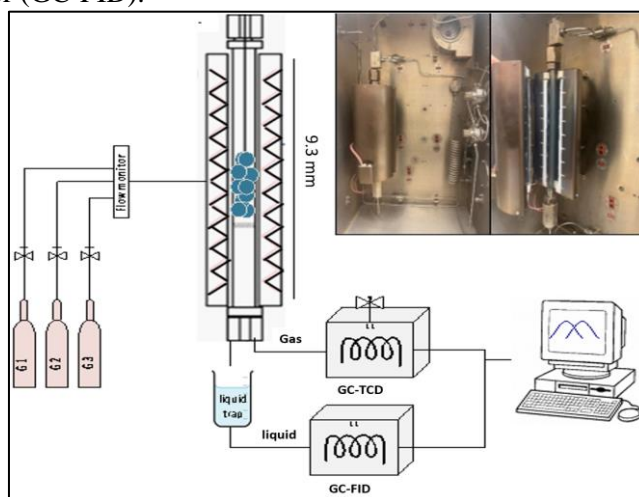


Figure 2. Schematic diagram of the experimental set-up

The CO_2 conversion was calculated using Equation (4):

$$\text{CO}_2 \text{ conversion (\%)} = \left[\frac{f_{\text{CO}_2}(\text{in}) - f_{\text{CO}_2}(\text{out})}{f_{\text{CO}_2}(\text{in})} \right] \times 100 \quad (4)$$

Where $f_{\text{CO}_2}(\text{in})$ and $f_{\text{CO}_2}(\text{out})$ are the CO_2 flow rates into and out of the reactor, respectively.

The selectivity of the products (methanol and CO) were calculated using Equations (5)-(6), respectively:

$$\text{CH}_3\text{OHs selectivity (\%)} = \left[\frac{n_{\text{CH}_3\text{OH}}}{n_{\text{Total product}}} \right] \times 100 \quad (5)$$

$$\text{CO selectivity (\%)} = \left[\frac{n_{\text{CO}}}{n_{\text{Total product}}} \right] \times 100 \quad (6)$$

Where n is the number of moles of considered compounds.

The methanol and CO yields in $\text{g}_P \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ were calculated using Equations (7) and (8), respectively:

$$\text{CH}_3\text{OH yield} = \left[\frac{\text{g}_{\text{CH}_3\text{OH}}}{\text{wt of catalyst (g)} \times \text{h}} \right] \quad (7)$$

$$\text{CO yield} = \left[\frac{\text{g}_{\text{CO}}}{\text{wt of catalyst (g)} \times \text{h}} \right] \quad (8)$$

3. Results and Discussion

3.1. Reactor performance

3.1.1. Effects of Cu loading on catalytic activity

The copper content is the most important element influencing the activity of Cu-based catalysts for conventional methanol synthesis. In this work, four catalytic materials with different compositions were synthesized. The effect of varying the active metal (Cu) loading was evaluated as three Cu-based catalysts with a composition of 10, 20, and 30% copper impregnated on similar base material of 10% CaO/ γ -Al₂O₃ were tested for methanol production under reaction conditions of T=300°C, P=60 bars, gas hourly space velocity (GHSV) of 5000 h⁻¹ and a CO₂/H₂ gas ratio of 3:1.

Obtained results presented in Figure 3, show that increasing Cu content in the catalyst composition had a minor effect on CO₂ conversion ranging from 15.08% to 16.44% with the following order: 20Cu10CaO > 10Cu10CaO > 30Cu10CaO with no considerable change between the catalysts containing 20% Cu and 10% Cu.

The effect of Cu content on CO₂ conversion can be related to Cu surface area, its dispersion, as well as the confined crystallization of copper nanocatalysts. The enhanced conversion of CO₂ with increasing Cu amount is ascribed to the higher mass fraction of CuO on the support as elaborated in XRD intensities (not shown here), potentially providing more Cu surface area. The obtained CO₂ conversion values might also be attributed to the support (10CaO/Al₂O₃) and its interface effect with the Cu metal. It is well known that the base material is a dominant factor that directly influences the reaction activity, which is basically achieved by forming a metal-support interface or active metal-support interaction [13]. We believe that the base material (10CaO/Al₂O₃) immobilizes Cu particles and enhances the active site dispersion and maintains high thermal stability [85]. Moreover, higher Cu loading affects the amount of CO₂ adsorbed, suggesting that the formed CuO has basic sites to adsorb CO₂. A similar phenomenon was observed by Din et al. [14],

Methanol selectivity and methanol space time yield (STY) as a function of Cu loading as shown in Figure 3 revealed that under the same reaction conditions indicated earlier, the order of methanol selectivity was found to be in the order of 20Cu10CaO > 10Cu10CaO > 30Cu10CaO with a similar trend for space time yield (STY). The catalyst (cat) containing 20% Cu has the highest methanol selectivity (18%) and higher STY (0.085 g_{MeOH} g_{cat}⁻¹ h⁻¹), whereas the catalyst with Cu loading of 30% had a methanol selectivity of 13.4% and STY of 0.06 g_{MeOH} g_{cat}⁻¹ h⁻¹, respectively. The decrement in methanol selectivity and STY for the case of catalyst with Cu loading of 30% might be attributed to the resulting copper sintering at the catalyst surface, owing to the agglomeration and accumulation of copper particles at higher loading. These results are in agreement with the findings reported by Karelavic et al. [15]. The selectivity and space time yield (STY) of carbon monoxide (CO) were relatively high and followed the opposite trend of methanol's selectivity and STY. The CO selectivity and STY passed their lowest values by the 20Cu10CaO catalyst followed by 10Cu10CaO and 30Cu10CaO catalysts, respectively.

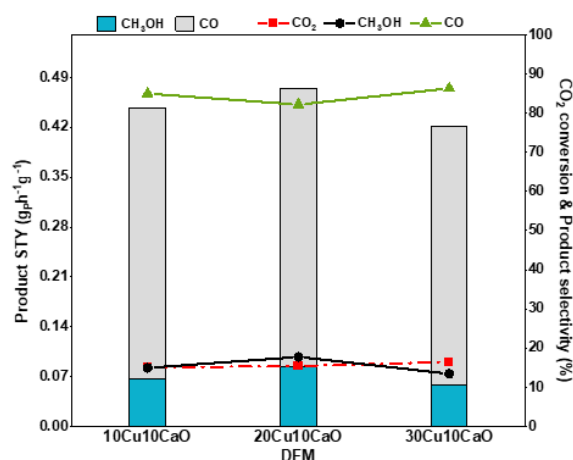


Figure 3. Effects of Cu loading on CO₂ conversion (%), CH₃OH yield (g_{CH₃OH} h⁻¹g_{cat}⁻¹) and selectivity (%), and CO yield (g_{CO} h⁻¹g_{cat}⁻¹) & selectivity (%).

3.1.2. Effects of adsorbent loading on catalytic activity

The effect of adsorbent loading on the material catalytic activity for CO₂ conversion was investigated under the same operating conditions using two different loading of adsorbent in the catalysts compositions. The CO₂ conversion, methanol selectivity, and CO selectivity were plotted as function of adsorbent loading as shown in Figure 4. It was found that with decreased adsorbent content from 10wt% to 5wt%, the CO₂ conversion rose from 15.4% to 18% respectively indicating that low CaO loading had a positive effect on CO₂ conversion. In fact, beside the copper active sites contribution, the adsorbent present in the catalyst also contributes to the overall performance of the catalyst. CO₂ is more easily absorbed by CaO while hydrogen is thought to be chemisorbed and spill over by the copper active sites.

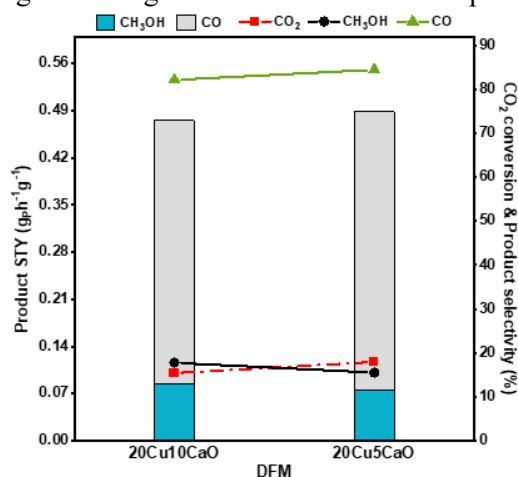


Figure 4. Effects of adsorbent loading on CO₂ conversion (%), CH₃OH yield (g_{CH₃OH} h⁻¹g_{cat}⁻¹) and selectivity (%), and CO yield (g_{CO} h⁻¹g_{cat}⁻¹) & selectivity (%).

It is reasonable to conclude that the 20Cu10CaO catalyst reduced activity is due to the stronger CO₂ adsorption force on the surface, which slows down CO₂ availability for the conversion reaction. The presence of excess adsorbent material may increase the interaction between adsorbed CO₂ and the adsorbent, making CO₂ more difficult to desorb and spill over onto the metallic sites. A minuscule decrease in the STY of methanol was observed for the 5% adsorbent loading catalyst which can be explained that higher CaO loading prevents proper Cu dispersion, resulting in poorer Cu dispersion on the catalyst surface.

4. Conclusions

The objective of this study was to assess the viability of using different Cu-based catalyst containing a CO₂ adsorbent for CO₂ conversion to methanol and other useful products. A series of novel Cu-based catalysts with CaO as adsorbents supported on alumina were synthesized and evaluated for CO₂ hydrogenation reaction. The freshly calcined catalysts were tested under constant operating conditions of T=300°C, P=60 bars, and GHSV=5000 h⁻¹. It was found that amongst the different catalysts, the 30Cu10CaO material achieved the highest CO₂ conversion of 16.5%. On the other hand, a maximum methanol selectivity of 17.8% associated with the lowest selectivity towards CO were obtained using 20%Cu-containing catalyst. Reducing CaO content in the prepared catalyst from 10% to 5wt% resulted in CO₂ conversion increase from 15.4% to 18% respectively.

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