Hydrogenation of CO\textsubscript{2} to methanol using Cu-based catalyst supported on oxide pellets

N H Berahim\textsuperscript{1}, A Abu Seman\textsuperscript{1}, N H Yasin\textsuperscript{1}, N S Abd Halim\textsuperscript{2} and N A Mohd Zabidi\textsuperscript{2}

\textsuperscript{1} Gas Sustainability Technology Department, PETRONAS Research Sdn Bhd, Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan Institusi Bangi, 43000 Kajang, Selangor.
\textsuperscript{2} Department of Fundamental and Applied Sciences, Institute of Contaminant Management, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia.

Email: hafizah.berahimjusoh@petronas.com

Abstract. Hydrogenation of CO\textsubscript{2} into methanol is one of the most economical process to reduce CO\textsubscript{2} concentration in the atmosphere. Since methanol is an industrial commodity used in chemical products as well as transportation fuel, this process has gained considerable interest, which enables the effective utilization of CO\textsubscript{2}. Nevertheless, the efficiency of direct CO\textsubscript{2} hydrogenation to produce methanol is strongly reliant on the activity of the catalyst. In this regard, the present work highlights the synthesis of methanol, catalytic evaluation and characterization of catalysts Cu/ZnO supported on Al\textsubscript{2}O\textsubscript{3} and SBA-15 pellets with the addition of group IV, V and VII metal oxides mixture as promoters. The catalysts were systematically prepared via impregnation technique with fixed Cu:Zn and promoter ratio from group VII:V:IV. The synthesized catalysts were characterized by H\textsubscript{2}-temperature-programmed reduction (H\textsubscript{2}-TPR), field emission scanning electron microscopy (FESEM), X-ray fluorescence (XRF), N\textsubscript{2} adsorption-desorption and N\textsubscript{2}O pulse chemisorption method. The crushing strength of the pellets were also tested. Catalytic performances were evaluated for methanol synthesis from CO\textsubscript{2} hydrogenation in a tubular, stainless steel fixed-bed reactor at 250 °C, 2 MPa, gas hourly space velocity (GHSV) 4000 ml/g.h and H\textsubscript{2}/CO\textsubscript{2} ratio of 3:1. The tri-promoted Cu/ZnO supported on Al\textsubscript{2}O\textsubscript{3} pellet resulted in CO\textsubscript{2} conversion of 13.3 % compared to 11.61 % from that of SBA-15-supported catalyst. However, the catalyst supported on SBA-15 pellet exhibited 54.59% methanol selectivity, whereas Al\textsubscript{2}O\textsubscript{3}-supported catalyst only resulted in 46.73 % methanol selectivity.

1. Introduction
When fossil fuels such as coal, oil and natural gas are used for power generation, massive volumes of greenhouse gas (GHG) are released into the atmosphere, often in the form of carbon dioxide (CO\textsubscript{2}) [1, 2]. Emission of high CO\textsubscript{2} to the environment has caused the mother earth to suffer from greenhouse effect. This later causing the earth climate to rise in temperature by ~1.5 °C in average on month-to-month basis [3]. As a requirement for future consumption, the production of sustainable and clean energy necessitates the use of energy-efficient and modern technology [4, 5]. The use of renewable H\textsubscript{2} to convert CO\textsubscript{2} into value-added products has proven to be an emerging approach for achieving this goal.
At present, there has been an immense effort in converting CO₂ directly to methanol. However, due to the limited equilibrium conversion of CO₂ to methanol at high temperatures, developing effective catalysts to break the thermodynamic barriers is critical. To improve methanol synthesis, a selective catalyst is necessary [7]. Hence, catalyst development for methanol synthesis from CO₂ hydrogenation is still considered as a research gap to be filled.

Since the beginning of the century, there has been a lot of interest in methanol synthesis. This is because of its importance in industrial processes as well as its prospects as a cleaner energy bearer [8]. Being a useful intermediate chemical, methanol yields product such as formaldehyde, dimethyl ether (DME), acetic acid in addition to its use as a primary fuel [9]. Traditionally, methanol has been produced catalytically using various oxide catalyst such as mixed Cr₂O₃-ZnO material and the process took place at high temperature and pressure using natural gas as the feed stock. Methanol synthesis was then innovated by adapting Cu/ZnO catalyst and operated at a much lower temperature and pressure [9]. Since then, catalysts for methanol synthesis are being developed industrially by adding other additives as well in the effort to control the sintering effect of Cu and deactivation of catalyst.

According to S.H Kang et al., addition of Al₂O₃ as the third component of Cu-based catalyst helps to disperse and stabilize the Cu/ZnO structure and also prevents the Cu from agglomeration due to the long term process [10]. Although Al₂O₃ has been widely used throughout the industries as it is rather non-expensive and easy to use. The acidic sites of Al₂O₃ can lead to the formation of dimethyl ether (DME) which is non-desirable for methanol synthesis reaction [11]. Apart from that, Al₂O₃ has a low surface area (350 m²/g), which leads to activity loss throughout catalytic reactions. One of its major drawbacks is its wide pore size distribution (3-15 nm) [12].

An ordered mesoporous structure such as SBA-15 has shown significant potential for material production especially in response to a vast range of environmental and technical demanding [13]. The advancement of SBA-15 ordered mesoporous structure, which is optimized with normal channel systems, well-defined pore size distribution, long-range ordering, and good thermal stability, has also led to advancements in the chemistry and catalysis fields [14]–[16]. The aim to synthesize and apply this solid have gained much attention in order to understand the templating mechanism and exploring its potential.

Metals from group IV, V and VII were incorporated together into the catalyst formulation as they act as structural stabilizer that prevents Cu nanoparticles from sintering. Addition of the mixture of metal promoter increase the basic property of the catalyst that later helps to increase the CO₂ adsorption throughout the reaction [17]. Addition of the metals also led to the formation of new active sites as a result of the increased in metal-support interaction [18]. In this work, combination of metal precursors, Cu/ZnO with promoters from transition metal groups were impregnated on Al₂O₃ and SBA-15 pellet to study effect of each pellet as support to the performance of methanol synthesis from CO₂ hydrogenation reaction.

2. Methodology

2.1. Preparation of Catalyst Pellet Support (Al₂O₃ and SBA-15)

All catalyst supports were pretreated in the tube furnace under Argon flow at temperature 400 °C for 5 hours to remove moisture and impurities.

2.2. Preparation of Cu/ZnO based Catalyst with the Addition of Tri Promoters

15 wt.% of Cu/ZnO with ratio of (70:30) and 3 wt.% of promoters (GVII/GV/GIV) (the specific salts for each group can’t be revealed at this stage of study) with ratio of (1:1:1) were synthesized using wetness impregnation method. The amount of each precursor and promoter added were calculated based on the amount of total catalyst mass being prepared. Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), Group VII salt, Group V salt, and Group IV salt were dissolved in deionized water to produce an aqueous solution. The solutions were stirred for 2 hours at room temperature. Then, the prepared aqueous precursor solutions were added dropwise into a beaker
containing the pellet supports (Al₂O₃ and SBA-15). No further stirring is required to avoid breakage of the pellet. The impregnated samples were dried at room temperature for 24 hours and calcined at 350 °C for 4 hours. The catalyst samples were denoted as CZ(M)A for Cu/ZnO/GVII/GV/GIV/Al₂O₃ and CZ(M)S for Cu/ZnO/GVII/GV/GIV/SBA-15. M represents the tri-promoters (GVII/GV/GIV).

2.3. Catalyst Characterization
Reduction study was conducted by Temperature Programmed Reduction (TPR) using a Thermo Finnigan TPD/R/O 110 CE equipped with a thermal conductivity detector (TCD). The catalyst was put in the quartz tube and pre-treated with pure N₂ at 250 °C with a holding time of 1 hr for moisture and impurities removal. The analysis subsequently continued by switching the gas flow to 5 % H₂/Ar (20 mL/min) to a maximum temperature of 950 °C with ramping rate of 10 °C/min and held for an hour. The hydrogen consumption is monitored by a thermal conductivity detector (TCD).

The morphology of the synthesized catalyst was observed using Hitachi SU8000 field emission scanning electron microscope (FESEM).

Textural analysis was performed on a Micromeritics ASAP 2020 analyzer by measuring the nitrogen adsorption/desorption isotherms at -196 °C. Prior to analysis, the sample was degassed at 350 °C with heating rate 10 °C/min. The adsorption data were used to calculate the Brunauer-Emmett-Teller (BET) basic surface area (SBET) and pore volume (VP) while the Barrett-Joyner-Halenda (BJH) model was used to calculate the mean pore diameter (DBJH) of the isotherm desorption branch [19].

The bulk compositions of active metals impregnated onto the pellet support was determined using XRF method. 3.0 g of calcined catalyst sample was put into the sample holder and the analysis were carried out based on calibration curves obtained using certified method (ASTM E1621).

The surface area of Cu and the degree of dispersion were determined using pulse chemisorption on a Micromeritics Autochem II 2920. The process involved two steps where the first step was reduction of the active metal to Cu⁰. Second step involved the injection of the known and constant doses of the reactive gas (N₂O). Injection process continued until it became saturated. With an appropriate calibration, amount of the exact reactive gas used to oxidize the copper surface can be determined which eventually lead to the quantification of the Cu dispersion and surface area.

2.4. Catalytic Performance Evaluation
CO₂ hydrogenation reaction was performed in a stainless steel fixed-bed reactor (PID Eng & Tech). The catalysts were reduced in-situ at atmospheric pressure with 5 vol% H₂ in He for 2 hours. After the reduction, the reactor tube was pressurized with He to 2 MPa, then switched to feed gas containing CO₂ and H₂ at a molar ratio of 1:3. The reaction temperature was set at 250 °C for 5 hours with GHSV 4000 ml/g.h [20] and the reactor effluents were analyzed using an on-line gas chromatograph (GC) outfitted with a thermal conductivity detector (TCD) and flame ionization detector (FID). The CO₂ conversion and MeOH selectivity were used to assess the catalytic activity.

3. Results and Discussion

3.1. The Reduction of Catalysts
The reduction of the modified catalysts was determined using H₂-TPR profiles, as shown in figure 1. CZ(M)A showed two reduction peaks; a low temperature peak at 366 °C (α peak) due to the reduction of widely distributed CuO surface species, and a higher temperature peak at 566 °C (β peak) owing to the reduction of bulk-like CuO [21, 22]. While for CZ(M)S, the catalyst showed a large reduction peak in the 200 °C to 500 °C region that could originate from the Cu species and other precursor salt species. Table 1 results for CZ(M)S indicates a main reduction peak at 383 °C and a shoulder at 631 °C. The CZ(M)S exhibited an intense and broader peak compared to CZ(M)A. This phenomenon might be due to the support difference and the uniform crystallite size of Cu dispersed on SBA-15 support [23]. Furthermore, the broader peak could also relates to the higher active site exposed to the H₂ where the
The surface area of the CZ(M)S is higher than that of CZ(M)A as presented in Table 2. The catalysts were reduced at 400 °C before the CO₂ hydrogenation reaction.

![TPR Profile CZ(M)A vs CZ(M)S](image)

**Figure 1.** H₂-TPR profiles of CZ(M)A and CZ(M)S.

**Table 1.** TPR quantification data for CZ(M)A and CZ(M)S.

| Catalyst | H₂ Consumption (µmol/g) | Reduction Temperature Peak (°C) |
|----------|-------------------------|---------------------------------|
|          |                         | T1     | T2     |
| CZ(M)A   | 411.12                  | 366    | 566    |
| CZ(M)S   | 1258.75                 | 383    | 631    |

3.2. **Morphology**

FESEM images of Al₂O₃, CZ(M)A, SBA-15, and CZ(M)S are shown in Figure 2. All samples had an irregular shape, however for the impregnated samples, agglomeration can be observed. The catalysts, CZ(M)A and CZ(M)S contained particles which were distributed onto the supports and filled the pores, which led to the reduction in the surface area of the samples, as reported in Table 2 [24].
3.3. Textural and Physical Properties

Table 2 displays textural properties, namely catalyst surface area ($S_{BET}$), pore volume ($V_p$) and pore diameter ($D_{BJH}$). SBA-15 and loaded catalyst CZ(M) supported on SBA-15 have the highest BET surface area of 447.01 and 339.17 m$^2$/g, respectively compared to those of Al$_2$O$_3$ and its CZ(M) supported catalyst. The loaded samples show slightly lower values of BET surface area and pore volume compared to those of bare supports which indicated that the impregnated metals have occupied the pores of the bare support. On the other hand, an opposite trend was observed on the diameter of the pores. The incorporation of active metals precursor into the pores of the support decreased the surface area and pore volume, however this incorporation leads to the internal pore strain thus increasing the pore diameter [25].

Table 2. Textural properties of the catalysts.

| Sample    | $S_{BET}$ (m$^2$/g) | $V_p$ (cm$^3$/g) | $D_{BJH}$ (nm) |
|-----------|----------------------|------------------|----------------|
| Al$_2$O$_3$ | 341.52               | 0.46             | 4.25           |
| CZ(M)A    | 302.96               | 0.43             | 4.32           |
| SBA-15    | 447.01               | 0.49             | 3.77           |
| CZ(M)S    | 339.17               | 0.41             | 3.83           |

Table 3 displays the XRF analysis for the bulk compositions of the impregnated active metals. The prepared catalysts at Cu to Zn ratio of 7:3 were impregnated on the pellets with 15 wt.%, while all the tri promoters (M), were loaded with 1 wt.% each. The outcome of XRF analysis were different from the expected value by which theoretically, the amount of Cu should be about 10.5 wt.%, Zn 4.5 wt.% and tri promoters (M) at 1 wt.% each, indicating that the impregnation method did not result in homogeneous metal deposition on the pellet surface.
3.4. Chemisorption Analysis

Table 4 shows the findings of \( \text{N}_2\text{O} \) pulse chemisorption. The Cu surface area as well as the dispersion of the active sites over the support were affected significantly by the type of the oxide carriers. The CZ(M)A catalyst exhibits higher Cu metal dispersion (0.50 %) and Cu metal surface area (0.34 \( \text{m}^2/\text{g} \)) as compared to those of CZ(M)S catalyst which indicated a more homogeneous distribution of copper particles on the \( \text{Al}_2\text{O}_3 \) pellet compared to that of SBA-15 support. In addition, the average particle size of Cu, \( d_{\text{Cu}} \), for CZ(M)A sample was found to be 209 nm, which is significantly smaller than the average particle size of 321 nm for the CZ(M)S sample. Cu particle size is a significant parameter of the catalyst in methanol hydrogenation reaction as smaller Cu particles increase the interfacial area with the adjacent metal oxide, thus enhancing the synergistic effect and increasing the catalyst's efficiency [26].

| Catalyst | Composition of support (wt. %) | Composition of active metals (wt. %) | Composition of promoters (wt. %) |
|----------|--------------------------------|-----------------------------------|---------------------------------|
|          | \( \text{Al} \) | \( \text{Si} \) | \( \text{Cu} \) | \( \text{Zn} \) | \( \text{GVII} \) | \( \text{GV} \) | \( \text{GIV} \) |
| CZ(M)A   | 82                             | -                                 | 11.16                           | 3.84                           | 1.67                               | 0.33                               | 1                               |
| CZ(M)S   | -                              | 82                                | 11.65                           | 3.35                           | 0.52                               | 1.15                               | 1.33                            |

Table 4. \( \text{N}_2\text{O} \) pulse chemisorption.

3.5. Catalytic Performance

Table 5 shows the catalytic performance of CZ(M)A and CZ(M)S catalysts in terms of \( \text{CO}_2 \) conversion (\( \chi_{\text{CO}_2} \)) and methanol selectivity (\( S_{\text{CH}_3\text{OH}} \)). Under the conditions of the catalytic test, it shows that, \( \text{Al}_2\text{O}_3 \)-supported catalyst, CZ(M)A resulted in higher \( \text{CO}_2 \) conversion of 13.30 % as compared to CZ(M)S at 11.61 %. Even so, an inverse trend was observed for methanol selectivity where CZ(M)S exhibited higher value than that of CZ(M)A at 54.59 % and 46.73 %, respectively. As reported by previous findings [27, 28], the determination of catalytic activity for Cu-based catalysts is heavily dependent on CuO particles, Cu surface area, and small crystallite size, which explains the higher activity exhibited by the CZ(M)A catalyst in terms of \( \text{CO}_2 \) conversion. Although the CZ(M)S has lower Cu surface area, lower Cu metal dispersion and large Cu particle size as compared to CZ(M)A, it is selective towards methanol formation. It is also well known that catalytic activity is heavily dependent on the interaction among Cu and oxide components for the Cu-based catalysts for methanol synthesis. Even though the CZ(M)S has higher surface area and pore volume, the \( \text{CO}_2 \) conversion is lower than that CZ(M)A. There is no clear connection between the accessibility factors (\( S_{\text{BET}} \) and \( V_p \)) and catalyst efficiency, which should be governed by other material properties [29, 30]. The methanol yield for both CZ(M)A and CZ(M)S are comparable at 6.22 % and 6.34 % respectively. It is hard to conclude at this preliminary stage, however, methanol selectivity is an important aspect to look at for this reaction as methanol is the targeted product which need to be maximized. In this case, CZ(M)S can be considered as the most efficient catalyst due to its high methanol selectivity. Even though CZ(M)A has higher \( \text{CO}_2 \) conversion, the amount of \( \text{CO}_2 \) converted to other products also high which concluded its lower methanol selectivity compared to CZ(M)S. Figure 3 and figure 4 show the time on stream of \( \text{CO}_2 \) conversion and methanol
selectivity for both catalysts. It was found that the reactions for both catalysts were stable over the time-
on-stream of 5 hours.

Table 5. Catalyst performance evaluation.

| Catalyst | $X_{\text{CO}_2}$ (%) | $S_{\text{CH}_3\text{OH}}$ (%) |
|----------|------------------------|-------------------------------|
| CZ(M)A   | 13.30                  | 46.73                         |
| CZ(M)S   | 11.61                  | 54.59                         |

reaction conditions: $T=250^\circ\text{C}$, $P=2$ MPa, $\text{H}_2$/$\text{CO}_2$ (volume ratio) = 3:1, and GHSV=4000 mL/(g·h)

Figure 3. CO$_2$ conversion time on stream profiles.

Figure 4. MeOH selectivity time on stream profiles.

4. Conclusion
In this study, Al$_2$O$_3$ and SBA-15 pellets were used as catalyst carriers for the tri-promoted Cu/ZnO catalyst. The catalyst reduction, its morphology, textural and physical properties were investigated. The catalytic performance for both CZ(M)A and CZ(M)S catalysts in a CO$_2$ hydrogenation reaction were evaluated under the same reaction conditions. The results show that CZ(M)A exhibited CO$_2$ conversion of 13.30 %, which was higher compared to that of CZ(M)S catalyst. However, the CZ(M)S catalyst was more selective towards methanol formation compared to the CZ(M)A catalyst. The methanol selectivity
obtained over the CZ(M)S and CZ(M)A catalysts were 54.59 % and 46.73 %, respectively. It is recommended that future work to focus on the optimization of the synthesis technique for the pellet catalyst which will influence its’ physicochemical properties. Process reaction optimization such as temperature, pressure, feed ratio and GHSV will also provide a larger picture on the catalytic performance evaluation. Catalyst deactivation study can also be part of the future work to determine the longevity of the catalyst in the reaction.

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