Effects of calcination temperature on the catalyst performance in a CO2 hydrogenation reaction

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Abstract: Cu/ZnO catalysts were synthesized on Al2O3-ZrO2 support via impregnation method with addition of manganese and niobium promoters. Samples were calcined at 181, 350 and 518 ºC. Different characterization techniques such as H2-TPR and CO2-TPD were used to study the catalytic reduction behavior and catalytic basicity, respectively. H2-TPR studies shows that all the catalysts reduction occurred on the range of temperature between 237 ºC and 265 ºC. The CO2-TPD profiles showed that the calcination temperature significantly influences the basicity of the catalyst and the catalyst calcined at 350 oC was proved to contain the highest amount of the basic sites. Furthermore, the characterization results were validated through analyzing of the catalytic performance during CO2 hydrogenation reaction and the results indicate that highest methanol yield of 12.2 % were obtained from the catalyst that calcined 350 oC.

Keywords: Methanol, CO2 Hydrogenation, calcination temperature

1. Introduction

Methanol, also known as wood alcohol was commercially obtained from destructive distillation of wood before mainly produced by hydrogenation of carbon monoxide (Equation 1). At room temperature, methanol exists as a polar colorless, volatile, and flammable liquid form. Methanol, being the simplest type of alcohol, has a distinctive odor similar to the drinking alcohol, ethanol but far more toxic than ethanol [1]. Despite that, methanol has been identified as a precursor to other commodity chemicals such as acetic acid, dimethyl ether, and methane, hence, more than 20 million tons of methanol is being produced annually for these industrial demands[2]–[4].

\[
\begin{align*}
\text{CO} + 2\text{H}_2 & \rightarrow \text{CH}_3\text{OH} \quad (1) \\
\text{CO}_2 + 2\text{H}_2 & \rightarrow \text{CH}_3\text{OH} + 2 \text{H}_2\text{O} \quad (2)
\end{align*}
\]

In this era, the significant increase of CO2 content in the earth’s atmosphere develops researchers’ interests to produce valuable chemicals from CO2, such as methanol, as shown in equation 2 [5]–[7]. This process is one of the best options for storing energy in a most convenient form of liquid fuels with sufficiently high energy density in comparison to all the existing methods of energy storage [8]. However, this process is also very challenging due to the high stability of the CO2.

Commercially, methanol is synthesized from syngas feedstock using Cu/ZnO/Al2O3 catalyst [9]. Besides the commercialized alumina support, zirconia (ZrO2) is utilized as one of main catalyst components because of its strength and thermal-resistant property. Findings by Witoon et al. suggests that CO2 hydrogenation is highly influenced by the zirconia phase. Cu-ZrO2 interaction of amorphous-ZrO2 and tetragonal-ZrO2 is stronger than monoclinic-ZrO2[10]. A study conducted by Zhang et al. proved that the presence of ZrO2 in the commercial CO2 hydrogenation catalyst has increased the CO2 conversion up to 25.9–24.7% at 250 ºC and 5 MPa using 10% of alumina sol in a slurry bed reactor [11]. Recently, ZrO2 also found to reduce weak basic sites which resulted in high methanol selectivity (75%) over the CuO-ZnO catalyst which was calcined at temperature >600°C [12].

Besides ZrO2, manganese (Mn), zirconium (Zr), titanium (Ti), lead (Pb), etc. also exhibit ability to fine-tune interfaces between their oxides and active copper which promote methanol selectivity and the stability of the catalyst[13]–[17]. For instance, TiO2, ZrO2, and TiO2-ZrO2 mixed-oxide on CuO-ZnO catalyst have been reported to improve the CuO dispersion and increase the Cu surface area and adsorption capacities of CO2 and H2 [18] - [19].

This study investigated the roles of calcination temperatures on physiochemical properties of Mn and Nb-
promoted Cu/ZnO/Al2O3-ZrO2 catalyst and their performance in CO2 hydrogenation reaction into methanol. The synthesized catalysts were characterized with field emission scanning electron microscope (FESEM), hydrogen temperature-programmed reduction, H2-TPR, and carbon dioxide temperature-programmed desorption (CO2-TPD) techniques.

2. Methodology (Experimental)

2.1. Catalyst Synthesis

The catalyst was prepared using an impregnation method with 15 wt% metal loading at Cu to ZnO ratio of 7:3. A total of 0.09% of Mn and Nb metals were incorporated into the catalyst as promoters. For synthesis of 10g catalyst, 0.021g of Mn(NO3)2.4H2O [Merck], 0.014g of C4H4NNbO9 [Merck], 3.995g of Cu(NO3)2 [Merck], and 1.644g of Zn(NO3)2 [Sigma Aldrich], were dissolved in deionized water and stirred for 1 hour and then added dropwise onto the Al2O3-ZrO2 [SASOL] powder. The mixture was continuously stirred for 24 hours and the pH was maintained at 7 using 10% ammonia solution, NH4OH [Merck]. Then the mixture was filtered and the sample was washed using deionized water. The sample was dried at 120ºC for 12 hours and then calcined statically at the presence of air for 4 hours under different range of temperature 181, 350 and 518 ºC to study the effect of the calcination temperature on the catalytic performance.

2.2. Catalyst Evaluation

Catalyst evaluation was performed in a fixed-bed reactor (Microactivity Reference, PID Eng Tech). Prior to the reaction, a 0.2g of sample was treated in 5 vol% of H2 in Argon gas at 20 mL min−1 for 2 hours. The CO2 hydrogenation reaction was performed at 22.5 bar, 250ºC, and 1:3 of CO2:H2 with a total flow rate of 36 mL/min for 5 hours. The reactor effluents were analyzed using a gas chromatograph (Agilent 7890A) equipped with a TCD detector for H2 and CO2 analysis, and FID detector for analysis of alcohols and other hydrocarbons [20]. CO2 conversion, alcohol selectivity and methanol yield were calculated using Equation 1, equation 2, and equation 3, respectively.

\[
\text{CO}_2 \text{ conversion (\%)} = \frac{\text{Mole of CO}_2 \text{ in} - \text{Mole of CO}_2 \text{ out}}{\text{Mole of CO}_2 \text{ in}} \times 100
\]

\[
\text{Methanol selectivity (\%)} = \frac{\text{Mole of methanol produced}}{\text{total mole of product}} \times 100
\]

\[
\text{Methanol yield (\%)} = \frac{\text{CO}_2 \text{ conversion (\%)} \times \text{Methanol selectivity (\%)}}{100}
\]

2.3. Catalyst Characterization

The morphology was observed on a Hitachi-8020 field emission scanning electron microscope (FESEM) at 5K magnification. The reduction profile of the catalyst was studied via the hydrogen temperature-programmed reduction (H2-TPR) using a TPR equipment (1100 CE Instrument). 40-50 mg catalyst was placed in the quartz tube and was pre-treated at 250ºC with a ramping rate of 10°C/min under the flow of pure N2 for 1 hour. The analysis was then continued by flowing 5% H2/Ar (20 mL/min) and heated to 990ºC at 10°C/min for an hour. The carbon dioxide temperature-programmed desorption experiments (CO2-TPD) were conducted using the same instrument as H2-TPR experiments. The CO2-TPD experiments were carried out by placing 40-50 mg of the calcined catalyst in the quartz tube and was pre-treated at 250ºC with a ramping rate of 10°C/min under He flow (20 mL/min) for an hour. The CO2 sorption then continued by continuous CO2 flow at 10 mL/min for 30 minutes at 75ºC.

3. Results And Discussion

3.1. Morphological Properties Of The Catalyst

FESEM images for catalyst samples calcined at different temperatures are shown in Fig. 1. All catalyst samples exhibit irregular morphology. Increasing the calcination temperature from 181 to 518 ºC did not change the morphology of the samples.
Fig. 1. FESEM images of catalysts calcined at (a) 181 °C (b) 350 °C, and (c) 518 °C

Fig. 2 shows the H\textsubscript{2}-TPR profiles for catalyst samples calcined at 181, 350 and 518 °C. The amount of hydrogen consumed and the corresponding reduction temperature are shown in Table 1. Samples calcined at 181 and 350 °C exhibit two distinct TPR peaks, denoted as α and β, due to the stepwise reduction behavior of the Cu-based catalysts. The α peak resulted from the reduction of highly dispersed copper oxide species which are easier to reduce while the β peak is ascribed to the reduction of bulk-like CuO [7], [21]. The occurrence of reduction with shoulder peaks had also been reported previously in the literature[22]. The H\textsubscript{2}-TPR profiles show that reduction for the catalysts occurred between 235 °C to 265 °C. For the sample calcined at 518°C, only a single H\textsubscript{2}-TPR peak was observed at 237 °C, which suggest that at high calcination temperature the bulk-like CuO was reduced directly to Cu\textsuperscript{0} instead of the stepwise reduction process which also consumed the least amount of hydrogen (1123 µmol/g).
Effects of calcination temperature on the catalyst performance in a CO2 hydrogenation reaction

Table 1. H2-TPR data of catalysts

<table>
<thead>
<tr>
<th>Calcination temperature (ºC)</th>
<th>H2 consumption (µmol/g) peak</th>
<th>Reduction temperature (ºC)</th>
<th>H2 consumption (µmol/g) peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>β</td>
<td>α</td>
</tr>
<tr>
<td>181</td>
<td>1403</td>
<td>2 38</td>
<td>2 65</td>
</tr>
<tr>
<td>350</td>
<td>2875</td>
<td>2 48</td>
<td>2 60</td>
</tr>
<tr>
<td>518</td>
<td>1123</td>
<td>237</td>
<td>1123</td>
</tr>
</tbody>
</table>

Fig. 3 shows the CO2-TPD profiles of the catalysts and the data are shown in Table 2. The TPD peak at temperature <200ºC is related to the weak basic sites which were contributed by the weakly-held surface hydroxyl groups (-OH). The medium basic sites (200 ºC - 500 ºC) were attributed to metal oxygen pairs i.e. Cu-O, Al-O, Zn-O, Mn-O, Nb-O and Zr-O [23], [24]. The high temperature desorption peaks (above 500ºC) represent the strong basic sites that are associated with coordinatively unsaturated O2− ions (low coordination oxygen atoms) from partial breakup of metal-oxygen pairs [25]. The sample that was calcined at the lowest temperature (181 ºC) contained mostly medium basic sites (β). However, the sample that was calcined at 350 ºC exhibited weak, medium and strong basic sites and had the highest amount of basic sites (574 µmol/g). Nevertheless, the medium-strength basic sites disappeared when the calcination temperature was increased to 518 ºC and the total amount of basic sites also decreased significantly to 88 µmol/g.
Table 2. CO$_2$-TPD data for the catalysts

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>Total basic sites (µmol/g)</th>
<th>Peak Temperature (°C)</th>
<th>CO$_2$ consumption (µmol/g) peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T$_1$</td>
<td>T$_2$</td>
</tr>
<tr>
<td>181</td>
<td>268</td>
<td>-</td>
<td>451</td>
</tr>
<tr>
<td>350</td>
<td>574</td>
<td>152</td>
<td>440</td>
</tr>
<tr>
<td>518</td>
<td>88</td>
<td>154</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3. CO$_2$-TPD profiles of the catalysts

Table 3 shows the catalytic activity in a CO$_2$ hydrogenation reaction performed at reaction temperature of 250 °C and reaction pressure of 22.5 bar. The values of CO$_2$ conversion ranged from 6.5 to 16% while the methanol selectivity varied from 19.5 and 75.9% using catalysts that were calcined at various temperatures. The highest methanol yield (12.2%) was achieved using a catalyst that was calcined at 350 °C. The catalytic activity is proved to be affected by the presence and the amount of the basic sites. Compared to the other catalysts, the sample that was calcined at 350 °C contained the highest amount of basic sites (574 umol/g) comprising weak, medium and strong basic sites which resulted in the highest catalytic activity. The sample that was calcined at high temperature (518 °C) might have been sintered and did not possess enough active sites to activate the CO$_2$ molecules, thus resulting in low CO$_2$ conversion. Our findings are in agreement with those of Shaharun et al. as they reported rapid catalyst weight loss starting below 200°C and continued up to 350°C for Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalyst [26]. Fig. 4 shows effects of catalysts’ calcination temperature on the yields of methanol in a CO$_2$ hydrogenation reaction. Based on this trend, 350 °C was found to the suitable catalyst calcination temperature that results in higher conversion, selectivity and methanol yield.

Table 3. Catalysts performance in a CO$_2$ hydrogenation reaction at 22.5 bar, 250 °C for 5 hours.

<table>
<thead>
<tr>
<th>Run</th>
<th>Calcination temperature (°C)</th>
<th>CO$_2$ conversion (%)</th>
<th>Methanol selectivity (%)</th>
<th>Methanol yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>181</td>
<td>6.5</td>
<td>19.5</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>16.0</td>
<td>75.9</td>
<td>12.2</td>
</tr>
<tr>
<td>3</td>
<td>518</td>
<td>7.2</td>
<td>58.4</td>
<td>4.2</td>
</tr>
</tbody>
</table>
Effects of calcination temperature on the catalyst performance in a CO2 hydrogenation reaction

Fig. 4. Effect of catalysts’ calcination temperature on methanol yields.

4. Conclusion

Effects of calcination temperature for Mn/Nb-promoted Cu/ZnO/Al2O3-ZrO2 catalyst have been investigated. All the catalyst exhibits irregular shape and reduced below 300 °C. The catalyst that was calcined at 350 °C exhibited the highest amounts of basic sites (574 umol/g) and resulted in the highest CO2 conversion (16.0%), methanol selectivity (75.9%) and methanol yield (12.2%).

5. Acknowledgement

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References


