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# Strategy to Prevent Reverse Reactions in Water Gas Shift (WGS) Through Cu/ZnO Catalyst with MFI Type of Zeolite Support

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**Abstract:** Water gas shift (WGS) reaction under medium temperature shift (MTS) conditions opens a new way to reduce CO content from dry methane reforming and to increase hydrogen productivity. This study aims to synthesize the Cu/ZnO/ZSM-5 catalyst for WGS reaction with high feed concentrations of H<sub>2</sub> and CO<sub>2</sub>. The reaction was carried out in a fixed bed reactor at atmospheric pressure, temperature 325 °C, and WHSV 60,000 ml/g-h using Cu/ZnO/ZSM-5 and Cu-based commercial catalyst. The Cu loading on the Cu/ZnO/ZSM-5 catalyst varied by 5, 10, and 15%-wt, while the commercial catalyst contained 58%-wt. According to the N<sub>2</sub> physisorption, Cu/ZnO/ZSM-5 catalyst has a pore size around 2 nm. H<sub>2</sub>-TPR shows the increase in metal loading on the Cu/ZnO/ZSM-5 catalyst causes the reduction peak shift to a higher temperature. The catalyst of Cu/ZnO/ZSM-5 with a Cu content of 15% resulted in a CO conversion of 18%, a yield of H<sub>2</sub> of 15%, and good stability for up to 8 hours. The presence of H<sub>2</sub> and CO<sub>2</sub> in the feed prevents the selectivity of the WGS reaction from reaching 100%. The increase in Cu metal loading increased the activity of the catalyst. The characterization was carried out to determine the physicochemical properties of the catalyst, namely, XRF, N<sub>2</sub> physisorption, and H<sub>2</sub>-TPR.

Keywords: Water gas shift; Cu-based catalyst; Medium temperature shift (MTS); ZSM-5; Hydrogen

## 1. Introduction

Indonesia has natural gas reserves, especially in the Natuna Sea, with a gas composition of 71 %-mol CO<sub>2</sub> and 28 %-mol CH<sub>4</sub><sup>1</sup>. Natural gas is still one of the world's main energy sources<sup>2</sup>. Natural gas with a high CO<sub>2</sub> content can produce hydrogen through the dry reforming

of methane (DRM). The adverse environmental impacts of CH<sub>4</sub> and CO<sub>2</sub>, notably global warming, highlight the advantages of the DRM<sup>3-5</sup>. The DRM gas product has an H<sub>2</sub>/CO ratio of around 1<sup>6,7</sup>. The presence of CO gas in the reforming product causes anode catalyst corrosion and poisoning and is incompatible with fuel cell systems<sup>8</sup>. Utilizing the water gas shift (WGS) reaction enhances

hydrogen production, decreasing CO emissions from DRM gas products. Hydrogen produced from the WGS reaction can be separated using Pd-based membrane to gain pure hydrogen as the final product<sup>9-14</sup>. Furthermore, after the separation/purification stages, hydrogen produced by WGS can be used as clean energy. Numerous research has been conducted to position hydrogen as a clean energy for the future<sup>15,16</sup>. One of the most significant sources for producing hydrogen gas is predicted to be biomass<sup>17</sup>. Energy holds significant importance in the diverse requirements across sectors, including industrial, transportation, and household needs<sup>18,19</sup>.

WGS reaction is a mildly exothermic process involving the reaction of CO and H<sub>2</sub>O<sup>20,21</sup>. Conventionally, the WGS reaction is carried out in two stages, namely, high-temperature shift (HTS) and low-temperature shift (LTS)<sup>22</sup>. Medium temperature shift (MTS) conditions were developed to minimize operating costs. Active metals play a crucial role in the catalysts employed in the WGS reaction<sup>23</sup>. Copper, one of the most significant industrial commodities, has a big influence on the world economy and catalyst<sup>24</sup>. The development of Cu-based catalysts under MTS conditions has been investigated at temperatures of 250–390 °C. The Cu catalyst was chosen because it is more economical than noble metals, easy to obtain, and shows promising activity in the WGS reaction<sup>25,26</sup>. In the form of oxide, copper oxide (CuO) can be utilized as a catalyst because it is a p-type semiconductor oxide, cheap, non-toxic, and stable photochemically<sup>27</sup>. Under MTS conditions, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst with 20%-wt Cu loading shows the best activity at a reaction temperature of 300 °C<sup>28</sup>, while Cu/CeO<sub>2</sub> catalyst shows the best activity with a Cu loading of 5%-wt at a temperature range of 300–390 °C<sup>26</sup>. These studies previously reported the activity of catalysts in MT-WGS reaction, but a major challenge is developing WGS catalysts to process DRM gas products in the MTS reaction.

Apart from the catalyst's active phase, the support is also important in facilitating the dispersion of the active phase on the catalyst's surface and within its pores. The support used in the WGS reaction is expected to have acidic properties to increase CO adsorption on the catalyst so that the overall reaction rate of WGS becomes higher<sup>29</sup>. ZSM-5 has a surface area of ~350 m<sup>2</sup>/g, stable at high temperatures, is acidic, and has a uniform pore size of 0.54–0.56 nm<sup>30,31</sup>. The use of ZSM-5 as support in Cu/ZnO-based catalysts has been investigated for the WGS reaction<sup>32,33</sup>. Based on Ayodele's preliminary study<sup>34</sup>, Cu/ZnO/ZSM-5 shows prospects in preventing the reverse WGS, which is characterized by the absence of CO formation in the product due to the acidic nature of ZSM-5 so further research is needed regarding the development of this catalyst in WGS reaction.

This research aimed to synthesize the Cu/ZnO catalyst over ZSM-5 support and to investigate the impact of

varying Cu loading for WGS reaction under MTS conditions within a fixed bed reactor. The feed composition consists of DRM gas products which contain CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>.

## 2. Materials and Methods

### 2.1 Catalyst Synthesis

ZSM-5 powder was purchased from Zibo Linxy Chemical, China (Si/Al: 25). Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Merck, ~99%-wt) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (HIMEDIA, ~99%-wt) that were used as the catalyst precursor without any pretreatment.

Cu/ZnO/ZSM-5 catalyst was synthesized using the impregnation method by adding the active phase precursor from Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and the promoter precursor Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O into the ZSM-5 support<sup>35</sup>. Coprecipitation and sol-gel are the other relatively low-cost<sup>36</sup> technique approaches in Cu-based catalyst synthesis. Unfortunately, the sol-gel synthesis process is lengthy and time-consuming, particularly the preparation of the gel<sup>37</sup>. The precursor solution was dripped slowly, and the impregnation was carried out for 4 hours at 70 °C under stirring<sup>34</sup>. After that, drying was carried out at 105 °C for 12 hours, followed by calcination at 350 °C for 4 hours with a heating rate of 10 °C/min. Calcination temperatures impacted the mechanical, microstructural, and physical features<sup>38</sup>.

### 2.2 Catalyst Characterization

Element compositions of catalyst were analyzed by X-ray fluorescence analysis (XRF)<sup>39</sup>. XRF was performed using the Orbis Micro-XRF Analyzer. The sample required for the XRF test is at least 200 mg. Surface area and pore size distribution were measured by BET and BJH methods via N<sub>2</sub> physisorption using Micromeritics Tristar II 3020. The catalyst sample was reduced using 5% H<sub>2</sub>/95% N<sub>2</sub> gas at a 30 ml/min flow rate at 30 to 600 °C with a heating rate of 10 °C/min.

### 2.3 Catalyst Activity Test

A fixed bed reactor was used for the WGS reaction under atmospheric pressure and at 325°C using 60 mg of catalyst and 300 mg of carborundum (SiC). First, purging was carried out using N<sub>2</sub> for 30 minutes. The catalyst reduction used 5% H<sub>2</sub>/95% N<sub>2</sub> gas for 1.5 hours (30 ml/min) and was followed by purging. A gas mixture of 25% CH<sub>4</sub>, 10% CO<sub>2</sub>, 15% CO, 50% H<sub>2</sub>, and steam was fed into the reactor with a steam/mixed gas ratio of 0.55 and a WHSV of 60,000 ml/g-h. The product gas is condensed to remove residual water. Gas products are analyzed using Perkin Elmer Gas Chromatography with a TCD detector every 20 minutes with time on stream (TOS) for 8 hours. The interpretation of the data carried out includes the following equation:

$$X_{CO} = \frac{F_{CO,i} - F_{CO,o}}{F_{CO,i}} \times 100\% \quad (1)$$

$$S_{CO_2} = \frac{F_{CO_2,o} - F_{CO_2,i}}{\beta} \times 100\% \quad (2)$$

$$S_{CH_4} = \frac{F_{CH_4,o} - F_{CH_4,i}}{\beta} \times 100\% \quad (3)$$

$$S_{H_2} = \frac{F_{H_2,o} - F_{H_2,i}}{\beta} \times 100\% \quad (4)$$

$$Y_{H_2} = \frac{F_{H_2,o} - F_{H_2,i}}{F_{CO,i} + F_{CO_2,i} + F_{CH_4,i}} \times 100\% \quad (5)$$

$$Y_{CH_4} = \frac{F_{CH_4,o} - F_{CH_4,i}}{F_{CO,i} + F_{CO_2,i} + F_{CH_4,i}} \times 100\% \quad (6)$$

\*notes: o= out, i= in, F= flow rate (mol/min)

X= conversion, S= selectivity, Y= yield

$$\beta = (F_{CH_4,o} - F_{CH_4,i}) + (F_{CO_2,o} - F_{CO_2,i}) + (F_{H_2,o} - F_{H_2,i})$$

### 3. Results

#### 3.1 Catalyst Characterization

Cu/ZnO/ZSM-5 catalyst was synthesized by impregnation method at 70 °C followed by drying at 105 °C for 12 hours and calcination at 350 °C for 4 hours. The actual metal content in each variation was confirmed by the XRF analysis presented in Table 1.

Table 1. Elemental composition from XRF.

Target Cu Loading	Composition (%-wt)				
	Cu	Zn	Si	Al	O
5%	4.89	4.73	53.45	1.66	35.28
10%	8.52	8.27	47.63	1.73	33.85
15%	10.29	9.92	45.01	1.67	33.11

Brunauer-Emmett-Teller (BET) and Barret-Joyner-Hallenda (BJH) methods were used to determine the surface area and pores of the catalyst. Analysis results are presented in Fig. 1, Fig. 2, and Table 2.

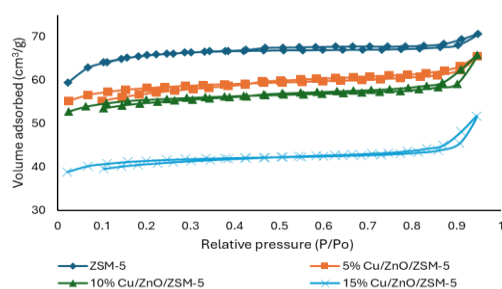


Fig. 1: N<sub>2</sub> Isotherm curve of Cu/ZnO/ZSM-5 catalyst.

The isotherm curves obtained are presented in Fig. 1.

At P/Po = 0–0.8, there was a steady increase in the adsorption volume, indicating a type I isotherm for microporous particles, but at P/Po = 0.8–0.95, there was a loop hysteresis which shows the isotherm type IV with the type of hysteresis H3. This confirms that the Cu/ZnO/ZSM-5 catalyst is a mesoporous particle<sup>40)</sup>, due to the agglomeration<sup>41)</sup>.

Table 2. Physical properties of Cu/ZnO/ZSM-5 catalyst.

	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)
ZSM-5	206.86	0.110	2.12
5% Cu/ZnO/ZSM-5	182.16	0.102	2.23
10% Cu/ZnO/ZSM-5	172.88	0.102	2.36
15% Cu/ZnO/ZSM-5	129.95	0.080	2.47

The surface area and pore size of each catalyst presented in Table 2 show a decrease in surface area and pore volume due to increased loading of Cu and Zn metals impregnated into ZSM-5. This can happen because a higher amount of metal loading causes the pores of the catalyst to be closed due to metal particle accumulation in the mouth of the catalyst<sup>28,42)</sup>.

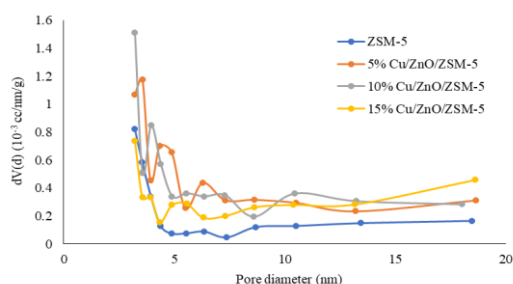


Fig. 2: Pore distribution profile of Cu/ZnO/ZSM-5 catalyst.

The pore distribution profile of the Cu/ZnO/ZSM-5 catalyst is presented in Fig. 2. The resulting pore diameter increases with metal loading. This phenomenon can be linked to a decrease in the catalyst's surface area. The smaller the surface area obtained, resulting larger the pore diameter. Furthermore, an increase in the catalyst's pore diameter at Cu metal loading of 10 and 15%-wt was attributed to two-stage calcination stages. Calcination that is carried out twice can cause the particles to agglomerate, making the pore diameter larger<sup>4,43)</sup>.

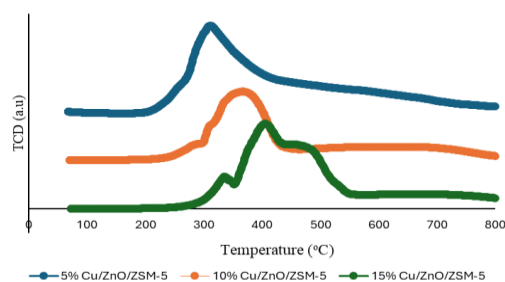


Fig. 3: H<sub>2</sub>-TPR profile of Cu/ZnO/ZSM-5 catalyst.

H<sub>2</sub>-TPR analysis was performed to determine the reduction behaviour of the catalyst<sup>44</sup>). The position of the resulting peaks is influenced by the dispersion of Cu, the interaction of Cu with the zeolite matrix, and the catalyst synthesis method used<sup>45</sup>). Reduction using hydrogen will result in the formation of Cu<sup>0</sup> and Cu<sup>+</sup> from copper oxide (CuO). The catalyst loading with 5%-wt and 10%-wt Cu metal produced a reduction peak in the temperature range of 200–400 °C, indicating a direct reduction of copper oxide to Cu<sup>0</sup>. This shows that the distribution of Cu particles on the catalyst is uniform<sup>33,46</sup>). The CuO reduction profile, characterized by broad peaks ranging from 200 to 400 °C, includes a two-step reduction of copper oxide, namely Cu<sup>2+</sup> to Cu<sup>+</sup> and Cu<sup>+</sup> to Cu<sup>0</sup> <sup>45</sup>). While the catalyst with 15%-wt Cu metal loading produced three catalyst peaks at temperatures of 330, 405, and 470 °C: the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>, CuO to Cu<sup>0</sup>, and Cu<sup>+</sup> to Cu<sup>0</sup>. The higher loading of Cu metal can cause a broadening of the peaks in the TPR profile<sup>46</sup>). The increase in metal loading on the Cu/ZnO/ZSM-5 catalyst causes the reduction peak shift to a higher temperature<sup>26</sup>). The impregnation method causes more metal aggregations to form so the viscosity of the metal precursors during drying increases, and segregation tends to occur, which causes H<sub>2</sub> consumption for the reduction of copper oxide to be higher.

### 3.2 Catalyst Activity

The evaluation of catalyst activity was conducted using a fixed bed reactor at 325 °C, atmospheric, and a WHSV of 60,000 ml/g-h. The activity of the Cu/ZnO/ZSM-5 catalyst was compared to a commercial catalyst with the composition: 58.28%-wt Cu, 30.66%-wt Zn, 0.03%-wt Co, 0.02%-wt Mn, 7.75%-wt Si, and 3.25%-wt Al. The thermodynamics involving side reactions were employed as a reference, and a CO conversion of 99.7% was found. The CO conversion is presented in Fig. 4.

It is established that a high surface to volume ratio and quantum size are the sources of the catalytic characterizations<sup>47</sup>). In this research, the catalyst's activity was not influenced by surface area but rather by the quantity of the active phase present<sup>26</sup>). Commercial catalysts with a Cu content of 58%-wt showed the highest CO conversion of 28%, while catalysts 5, 10, and 15%-wt Cu/ZnO/ZSM-5 produced CO conversions of 11%, 14%, and 18%. Cu/ZnO/ZSM-5 catalyst showed good stability for 8 hours, while commercial catalyst showed a slight decrease in catalyst activity performance. Gunawardana et al. studied the stability of the Cu/Ce catalysts and found that the MTS-WGS reaction activity increased with increasing Cu loading. Also, Cu/Zn/Al catalysts for MTS showed the relative amount of Cu, Zn, and Al is the main factor to reach a high active and stable catalyst<sup>28</sup>).

The higher loading of Cu in the catalyst leads to an increase in its activity, indicating that Cu serves as the main active site in the WGS reaction. According to research conducted by Lang et al.<sup>48</sup>), a catalyst containing 5.5 wt% of Cu exhibited higher CO conversion than a

catalyst with 4.5 wt% of Cu. Therefore, it was inferred that a lower Cu content would lead to reduced CO conversion due to the limited availability of active sites required for the reaction to take place. Based on Fig. 3, the 15% Cu/ZnO/ZSM-5 catalyst shows the broadest TPR peak and indicates that the consumption of H<sub>2</sub> is the highest. The amount of H<sub>2</sub> consumed during TPR is directly related to the number of active sites in the catalyst, which are essential for catalyzing the WGS reaction<sup>49</sup>).

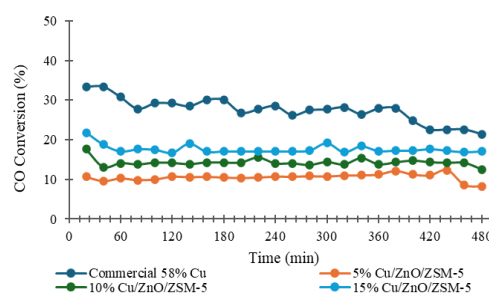
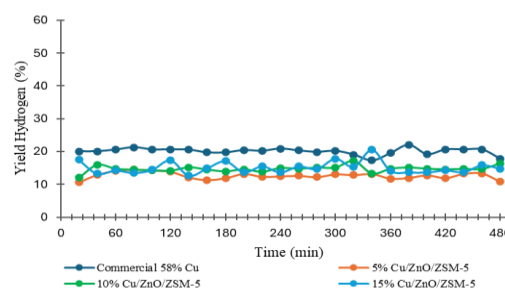
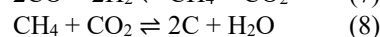
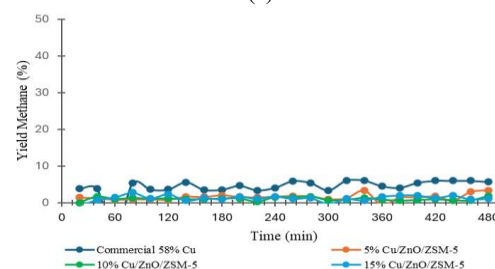


Fig 4: CO Conversion (325 °C, atmospheric for 8 h).

The potential occurrence of side reactions and the existence of CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> in the input also contribute to the reduced CO conversion. When CO<sub>2</sub> and excess H<sub>2</sub> are in the feed, CO conversion cannot reach equilibrium<sup>50</sup>). The existence of H<sub>2</sub> and CO<sub>2</sub> gases can initiate reactions leading to CH<sub>4</sub> (Eq.7), carbon (Eq.8), and the reverse WGS. CH<sub>4</sub> can be formed when H<sub>2</sub> reacts with CO at temperatures <600 °C<sup>51</sup>). Because of the side reactions, the selectivity of the resulting WGS reaction is not 100%. The yield and selectivity of the product are presented in Fig. 5 and Fig. 6.



(a)



(b)

Fig. 5: Yield (a) H<sub>2</sub> and (b) CH<sub>4</sub> (325°C, atmospheric for 8 h).

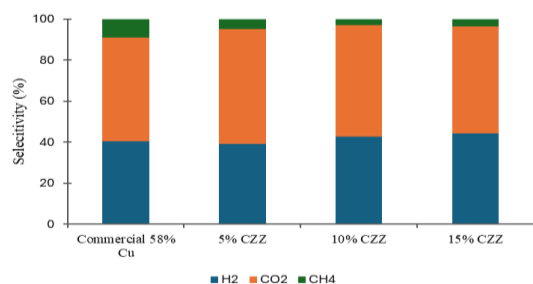


Fig. 6: Selectivity of the product (325°C, atmospheric for 8 h).

Based on Fig. 5, the commercial catalyst produces 20% H<sub>2</sub> yield, while the 5, 10, and 15%-wt Cu/ZnO/ZSM-5 catalysts produce 12%, 14%, and 15% H<sub>2</sub> yield, respectively. Commercial catalysts with a Cu content of 58%-wt show the highest CO conversion, but these catalysts show high selectivity to methanation with the highest CH<sub>4</sub> yield of 5%. This is supported by the selectivity calculation in Fig. 6, the selectivity for methanation of commercial catalyst is the highest (8.8%) compared to Cu/ZnO/ZSM-5 catalyst.

The formation of methane in all variations of Cu/ZnO/ZSM-5 catalysts was observed, but in very small amounts, and the yield of CH<sub>4</sub> obtained is smaller when compared to commercial catalysts. The presence of excess H<sub>2</sub> causes methanation, resulting in a low yield of H<sub>2</sub>, so the converted CO is not only used for WGS reaction but is also consumed for CH<sub>4</sub> formation as a side reaction. In a study on Cu-based catalysts, CH<sub>4</sub> production was observed at reaction temperatures below 500 °C when the H<sub>2</sub>/CO<sub>2</sub> feed ratio was  $\geq 3^{52}$ . Mikhailov et al.<sup>53</sup> investigated the use of Cu/ZSM-5 in the adsorption of CO and H<sub>2</sub> gases, and their findings reveal that Cu<sup>+</sup> in the zeolite binds CO more than H<sub>2</sub>. Using ZSM-5 as catalyst support in the WGS reaction, H<sub>2</sub> is not entirely adsorbed into the Cu/ZnO/ZSM-5 catalyst, which prevents methane formation.

#### 4. Conclusion

Cu/ZnO/ZSM-5 catalyst showed good stability for 8 hours. The higher loading amount of Cu metal increases the catalyst activity indicating that Cu acts as the main active phase. The best activity of the Cu/ZnO/ZSM-5 catalyst was obtained when the Cu loading was 15%-wt with a CO conversion value of 18%. A commercial catalyst with 58%-wt Cu produced the highest CO conversion, but a CH<sub>4</sub> yield of 5% was obtained, which indicates that the chance of a side reaction forming methane is high. The activity of WGS increased with increasing of Cu loading. In contrast, the 5% catalyst showed a higher surface area when compared to the areas of the higher Cu loading catalysts. It has been shown that BET surface area alone is not a main property for explaining WGS activity. The influence of the presence of excess H<sub>2</sub> and CO<sub>2</sub> in the feed triggers side reactions, especially the formation of CH<sub>4</sub> and reverse water gas shift reaction.

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