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Synthesis and Activity Test of Cu/ZnO/Al$_2$O$_3$ for the Methanol Steam Reforming as a Fuel Cell's Hydrogen Supplier

IGBN Makertihartha, Subagjo & Melia Laniwati Gunawan

Program Studi Teknik Kimia – FTI – ITB
Jalan Ganesha 10 Bandung 40132, Indonesia
Phone: +62-22-2500989, Email: makertia@che.itb.ac.id

Abstract. The synthesis of hydrogen from hydrocarbons through the steam reforming of methanol on Cu/ZnO/Al$_2$O$_3$ catalyst has been investigated. This process is assigned to be one of the promising alternatives for fuel cell hydrogen process source. Hydrogen synthesis from methanol can be carried out by means of methanol steam reforming which is a gas phase catalytic reaction between methanol and water. In this research, the Cu/ZnO/Al$_2$O$_3$ catalyst prepared by the dry impregnation was used. The specific surface area of catalyst was 194.69 m^2/gram. The methanol steam reforming (SRM) reaction was carried out by means of the injection of gas mixture containing methanol and water with 1:1.2 mol ratio and 20-90 mL/minute feed flow rate to a fixed bed reactor loaded by 1 g of catalyst. The reaction temperature was 200-300 °C, and the reactor pressure was 1 atm. Preceding the reaction, catalyst was reduced in the H$_2$/N$_2$ mixture at 160 °C. This study shows that at 300 °C reaction temperature, methanol conversion reached 100% at 28 mL/minute gas flow rate. This conversion decreased significantly with the increase of gas flow rate. Meanwhile, the catalyst prepared for SRM was stable in 36 hours of operation at 260 °C. The catalyst exhibited a good stability although the reaction condition was shifted to a higher gas flow rate.
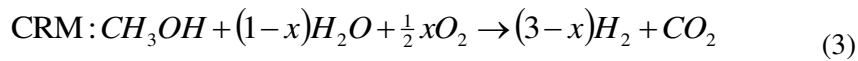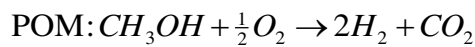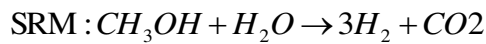
Keywords: *Cu/ZnO/Al$_2$O$_3$; fuel cell; hydrogen production; methanol steam reforming.*

1   Introduction

Fuel cell powered electric vehicles and power plants using hydrogen as fuel are currently being developed in an effort to protect the environment and sustainable development. Hydrogen produced by steam reforming of methanol (SRM) is an increasing worldwide interest, the equilibrium conversion of SRM reaction reaches around 100% at 150 °C at atmospheric pressure. Unfortunately, a considerable amount of CO (>100 ppm) as a by-product is produced during the reaction at temperature above 300 °C. As for the application of Polymer Electrolyte Fuel Cell (PEFC), even traces of CO (>20 ppm) in the reformed gases deteriorate the Pt electrode and the cell performance is worsened. An ideal method to produce hydrogen with lower amount of CO from SRM greatly

requires a high performance catalyst, which must be highly active and selective for hydrogen production and also stable for a long period in a continuous operation. Now the most widely used catalysts for this reaction are copper containing catalysts since copper has been found to be high activity and selectivity for hydrogen production [1, 2].

For fuel cell applications there are three processes available for extracting H_2 from methanol, namely: (i) steam reforming of methanol (SRM), (ii) partial oxidation of methanol (POM) and (iii) combined reforming of methanol (CRM). The reactions of these processes are given as follows:

$$SRM: CH_3OH + H_2O \rightarrow 3H_2 + CO2$$

$$POM: CH_3OH + \tfrac{1}{2}O_2 \rightarrow 2H_2 + CO_2$$

$$CRM: CH_3OH + (1-x)H_2O + \tfrac{1}{2}xO_2 \rightarrow (3-x)H_2 + CO_2 \tag{3}$$

The SRM reaction is a highly developed and thoroughly studied process and it is possible to produce a product gas containing up to 75% hydrogen while maintaining a high selectivity towards carbon dioxide. However, it is a slow and endothermic process. Therefore a significant amount of heat has to be provided to maintain the reforming reaction.

The SRM reaction is the reverse reaction of methanol synthesis from the mixture of hydrogen and CO_2 [1, 3, 4]. Hence, it is assumed that the catalyst for the methanol synthesis is also active for its reverse reaction. Traditionally, $Cu/ZnO/Al_2O_3$ is used to catalyze a low temperature gas shift reaction. Although the thermal stability of $Cu/ZnO/Al_2O_3$ catalyst is relatively low, its activity and selectivity are considerably high. Moreover, the raw materials to produce catalyst $Cu/ZnO/Al_2O_3$ could be found easily in Indonesia.

2   Experiment

2.1   Catalyst Preparation

A copper-based catalyst was derived from hydroxynitrate precursors prepared by impregantion of metal nitrates solutions in γ-Al_2O_3. In short, to prepare 10 gram of catalyst, 4.155 gram of $Cu(NO_3)_2.3H_2O$ and 1.755 gram of $Zn(NO_3)_2.4H_2O$ were needed. All these salts were diluted in 5.6 mL of aquadest. This volume of solution was determined from the pore volume of 8.361 gram of γ-Al_2O_3 catalyst support. The salts solution was impregnated into

γ-Al$_2$O$_3$ and then was dried at 120 °C for 12 hours. Afterward, the catalyst was calcined at 360 °C for 1 hour [5,6].

The characterization of CuO/ZnO/Al$_2$O$_3$ catalyst was carried out by means of XRD analysis in order to analyze the catalyst crystal structure, and BET isotherm adsorption to measure the catalyst surface area.

2.2   Activity Test

Hydrogen synthesis from methanol on Cu/ZnO/Al$_2$O$_3$ catalyst was carried out in the laboratory fixed bed reactor made of stainless steel with 8 mm internal diameter. For this experiment, 1 gram catalyst was used. Preceding of the reaction, the catalyst was reduced at temperature of 300 °C in the H$_2$/N$_2$ gas mixture for about 2 hours converted the CuO to Cu. The SRM reaction was carried out by means of introducing the gas mixture methanol-water with water to methanol ratio of 1.2. The total flow rate of gas was 20-90 mL/minute. In all experimental runs, the methanol concentration was kept at 17.8%. The reaction temperature was controlled at 200-300 °C. The experimental set up is shown in Figure 1. The gas products were analyzed by a Shimadzu gas chromatography. The GC was equipped with a thermal conductivity detector and two packed columns in parallel (one for separation of polar components i.e. CO$_2$, water, and methanol, and a molecular sieve for separation of H$_2$, O$_2$, N$_2$, and CO). The temperature of column was controlled at 50 °C. Argon was used as the carrier gas.
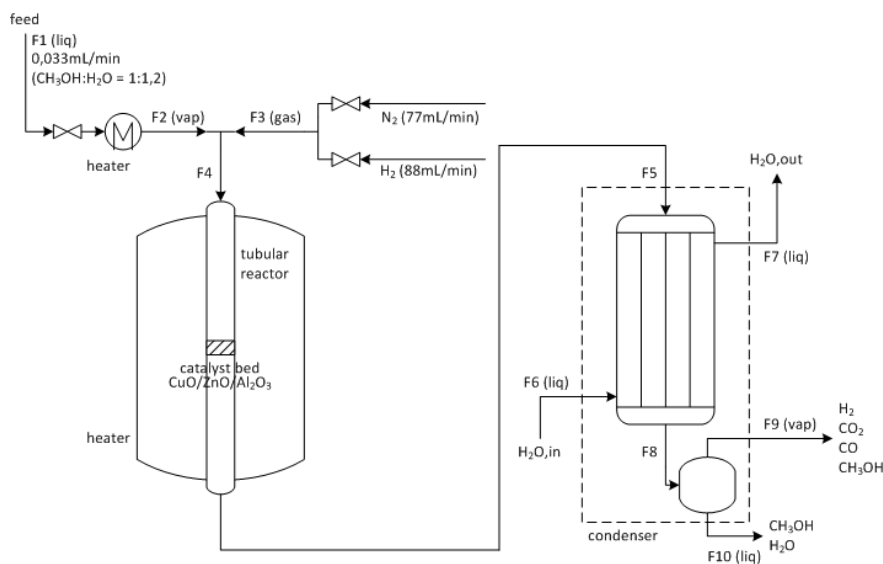

Figure 1 Process flow diagram of experimental set-up for SRM reaction [6].

3   Result and Discussion

3.1   Catalyst Characterization

The X-ray diffractogram of catalyst after calcinations is shown in Figure 2. The characteristic peaks of CuO and Al_2O_3 have been indicated in the diffractogram of catalyst after calcination. No other features are observed except the characteristic peaks of CuO appears at $2\theta \approx$ 36-38 ° indicating relatively large crystallites. This indicates that CuO is highly dispersed on the catalyst surface. Signals from crystalline ZnO were not detected due to a very small concentration of ZnO in the catalyst matrice, or the fact that ZnO is present in highly disorder or amorphous states because of the relatively low calcinations temperature (360 ^{o}C). However, features associated with Al_2O_3 were detected.
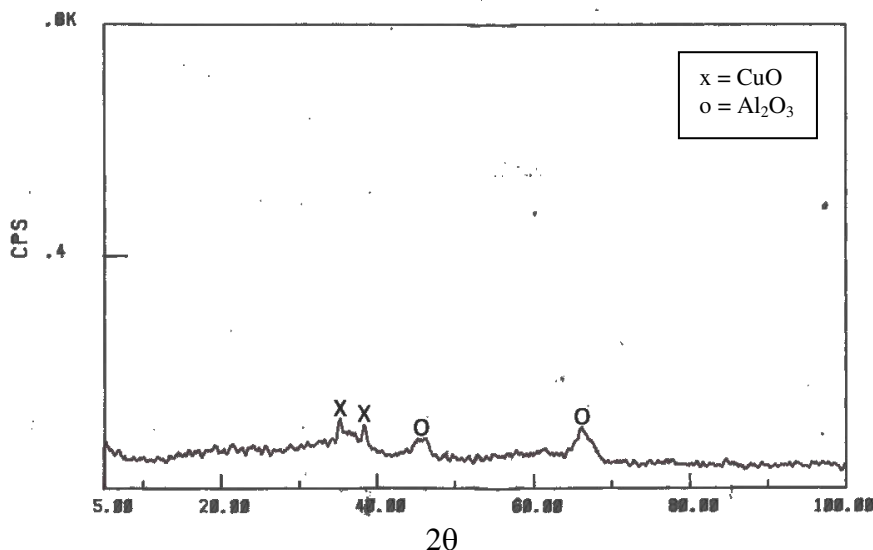

Figure 2   XRD difratogram of Cu/ZnO/Al_2O_3 catalyst.

The catalyst surface area was determined by BET (*Brunauer-Emmet-Teller*) method by means of using *Gas Sorption Analyzer NOVA 100 Quantachrome*. The catalyst surface area compared with the γAl_2O_3 are shown in Table 1.

Table 1   Catalyst specific surface area.

Sample	Specific Surface Area (m^2/g)
Cu/ZnO/Al_2O_3	194.69
γAl_2O_3	230

The γAl_2O_3 loosed 15% of its surface area due to the impregnation process with Cu and Zn species and heat treatment. However, this surface area was much greater than that of catalyst prepared by the co-precipitation method. A copper based catalyst prepared by Agrell et al (2003) by means of co-precipitation method has 92 m^2/g specific surface area. Most of copper based catalysts prepared by the co-precipitation method have specific surface area less than 100 m^2/g [7,8,9].

3.2   Catalyst Activity Test

Catalytic experiments were performed at atmospheric pressure in a laboratory packed-bed tubular reactor. The catalyst was diluted in glass wool to avoid adverse thermal effects. Both catalyst and diluents were sieved in order to minimize the pressure drop over the catalyst bed. The methanol and water mixture was fed to the evaporator by means of a liquid syringe pump. In this experiment, nitrogen was added as an inert. The reaction conditions are described in Table 2. One set of experiments was carried out under different weight hourly speed velocity (WHSV) and temperature but on a similar reactor setup.

Table 2   Reaction Conditions for Steam Reforming of Methanol

No	Parameters	Operating Conditions
1	WHSV	0.75-5 /hr
2	Heater	Voltage 5-10V 166°C-300°C
3	Methanol/Water	01:01.2
4	Reactor	id = 8 mm
5	Catalyst	1 gram
6	Tubular furnace	200-400°C
7	Pressure	atmospheric
8	Nitrogen	77 ml/min
9	Hydrogen	88 ml/min

Prior to each experiment, the catalyst was reduced in situ at 166–300 ∘C in a stream of 50% H_2 in N_2. The dwell time was at least 5 h in all cases. The temperature scheme of catalyst reduction is shown in Figure 3. The catalyst reduction aims to convert CuO to active metal Cu which is used for the reformation reaction of methanol.
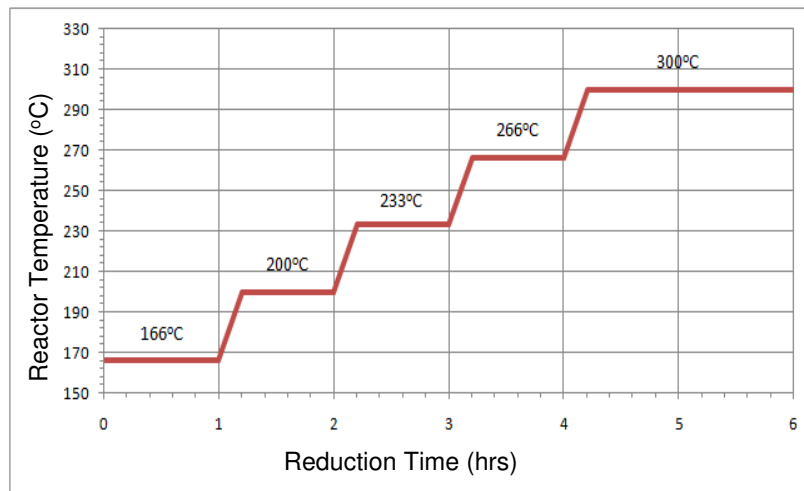
Figure 3 Temperature scheme for catalyst reduction.

The SRM experiments were conducted with steam in excess of stoichiometry (H_2O/CH_3OH = 1.2), ensuring the complete methanol conversion and suppressing the CO formation by the reverse water–gas shift (RWGS) reaction. The product gas composition was analyzed by a GC-8A Shimadzu gas chromatograph. In the following text, the product gas composition refers to the composition of the gas stream leaving the reactor, including unconverted methanol and O_2, but excluding N_2 used for dilution.

The catalytic activity was evaluated from the data collected between 5 h and 6 h of on-stream operation for methanol conversion (X(MeOH)), H_2 selectivity (S(H_2)), and CO_2 selectivity (S(CO_2)), and they are given as follows:

$$X(MeOH) = \frac{n(MeOH\ \text{conversion})}{n(MeOH\ \text{input})} \times 100\%$$
(4)

$$S(H_2) = \frac{n(H_2\ \text{out})/3}{n(MeOH\ \text{conversion})} \times 100\%$$
(5)

$$S(CO_2) = \frac{n(CO_2\ \text{out})}{n(CO_2\ \text{out}) + n(CO\ \text{out})} \times 100\%$$
(6)

3.2.1   Methanol Conversion

The catalyst activity was measured as a conversion of methanol in steam reformation reactor obtained from the concentrations of methanol in feed and product streams. Figure 3 shows the catalyst activity as a function of gas flow rate and reaction temperature. Analysis of the effluent gas indicated that H_2 and CO_2 were major components with a minor amount of CO. Other products such as formaldehyde, formic acid, methyl formate and dimethyl ether formed during reactions of methanol on Cu-based catalysts could not be detected under the reaction conditions.
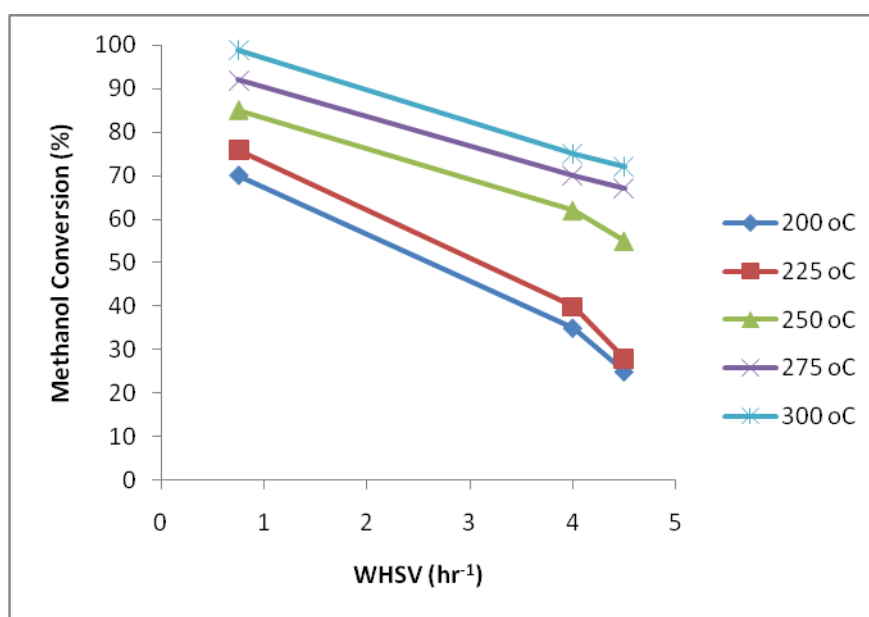

Figure 4   The catalyst activity in different WHSV and temperatures

Catalyst shows similar trend of activity in various reactor temperatures. The greater the WHSV, the smaller the methanol conversion obtained from the catalyst activity test. It is clear that the catalyst activity was a function of reaction temperature. Kinetically, the reaction rate is significantly influenced by the heat supplied by the reactor heater. Hence, at high temperature, the methanol conversion could be similar with the thermodynamic conversion. Above 275 °C, the SRM thermodynamic conversion is 100%. At 300 °C and low WHSV, the methanol conversion reached 99.8%.

3.2.2   Production of Hydrogen dan CO

Figure 4 shows the yield of hydrogen at various temperatures. The highest yield was given by the lowest WHSV at high temperature with the value close to the maximum expected according to the thermodynamic conversion. At temperature higher than 275 $^{\circ}$C, the production of CO was detected. However, the selectivity of CO_2 was still considerably high. At 275 $^{\circ}$C and 300 $^{\circ}$C, the selectivity of CO_2 were 97% and 94% respectively, resulting a high yield of hydrogen even at high reaction temperature. Above 300 $^{\circ}$C, the selectivity of CO will increase. Therefore the reaction temperature was kept below 300 $^{\circ}$C to restrain the production of CO.
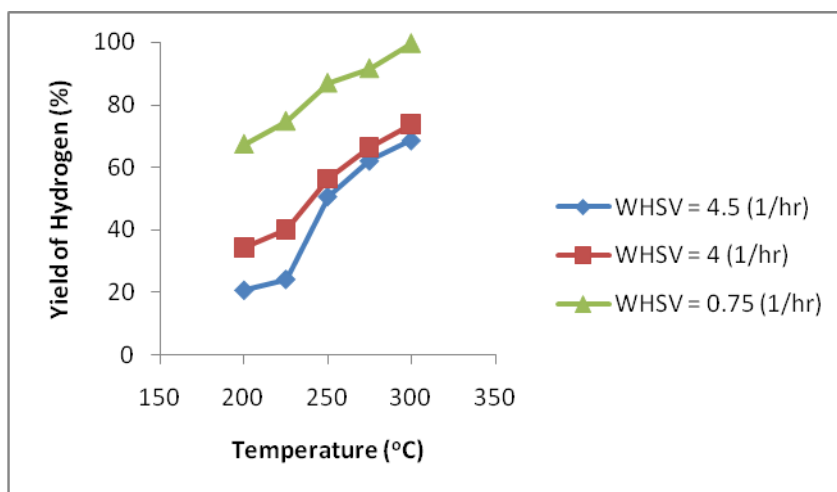

Figure 5   Yield of hydrogen at various WHSV.

Nevertheless, some studies reported that at temperature above 300 $^{\circ}$C, the hydrogen production rate of SRM catalyzed by $Cu/ZnO/Al_2O_3$ decreased [1,4,5] due to the carbon monoxide production at high temperature. In this condition, some side reactions producing carbon monoxide were favored. Furthermore, the profile of yield of hydrogen in SRM resulted from this experiment is similar with the profile observed by Turco, et al. [10].

CO is produced mainly from the reversed water gas shift reaction. With the presence of oxygen in the feed, CO is also produced from methanol decomposition, probably through the formation of intermediate oxygenated species, such as adsorbed formaldehyde or dioxymethylene that are bonded to metallic Cu or to cationic sites of the oxide matrix. These intermediate species are probably common also to the mechanism of SRM, and can be desorbed as gaseous formaldehyde or, if retained on the catalytic surface, further

dehydrogenated giving rise to CO or CO2. Thus it is expected that if the catalyst retains these intermediates strongly, it will favour the formation of CO. Turco *et al* observed that the production of CO increases with increasing aluminium content suggesting a correlation of CO with the acidity of the catalysts, in particular with the concentration of the strongest acid sites.The formation of CO was suppressed by means of using excessive water in the feed to avoid the reversed water gas shift reaction. At this reaction condition, the yield of hydrogen could also be decreased because of the reaction of methanol condensation producing formaldehyde, due to the acid sites of Al_2O_3 and/or aluminates. However, the condensation product was not detected. Hence, the yield of hydrogen was significantly decreased at higher WHSV mainly due to the lower methanol conversion at this reaction condition.
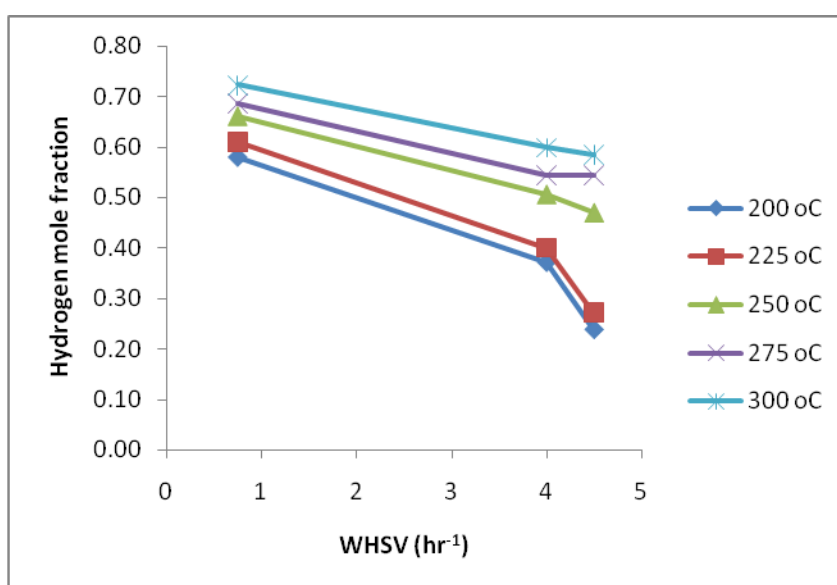

Figure 6 Hydrogen concentration in product gas at various WHSV and reaction temperature.

A comprehensive study related to production of CO in SRM has been reported by Purnama *et al* [4]. The level of CO produced in methanol steam reforming over copper-based catalysts can be influenced by the following factors: (i) reaction temperature, (ii) contact time, (iii) molar ratio of methanol and water, (iv) introducing oxygen to methanol–steam mixture, (v) particle size of the catalyst (intraparticle diffusion limitation), (vi) mechanical treatment of the catalyst, i.e. dilution, and (vii) heterogeneity of the copper surface resulting from defects in the Cu bulk or different morphology of the copper particles. Hence, with respect to the intraparticle diffusion limitation that influences the

amount of CO formed, the objective is to minimize the diffusion path. For packed bed reactors lower levels of CO can be achieved by using a very small particle size, where intraparticle diffusion limitation is absent. In this experiment, the catalyst powder was used in the reaction. Therefore the diffusion limitation was omitted, and the production of CO was suppressed. In such a reactor the grain size of the catalyst in the reactor plays an important role for the flow behavior. In order to achieve plug flow behavior of the gas through the catalyst bed, the diameter of the catalyst in general should be smaller than 0.1 times the inner diameter of the reactor. However, use of excessively small particles of catalyst in a reactor can increase the pressure drop across the reactor.

Accordingly, the hydrogen concentrations in product gas were evaluated. Figure 5 shows the quality of gas product at different WHSV and reaction temperatures. It can be observed that the product gas quality is favored at low WHSV and high reaction temperature. The highest hydrogen concentration is 0.72 mole fraction produced at 99.8% of methanol conversion. Meanwhile, the worst product gas quality was produced at temperature 200 ^{o}C. However, it was observed that the Cu/ZnO/Al$_2$O$_3$ catalyst used in this reaction was very selective to hydrogen production even at temperature 300 ^{o}C. It is probably due to a very good dispersion of metallic Cu phase on the catalyst support (Al$_2$O$_3$).

3.3   Catalyst Stability

Copper has a low Hüttig temperature [1], reflected by its relatively low melting point (1083 °C). It is well known that Cu/ZnO/Al$_2$O$_3$ catalysts suffer thermal deactivation at temperatures exceeding 300–350 °C. Therefore, some measures were taken in order to prevent deactivation of the catalysts in the present study. For instance, the catalysts were diluted with SiO$_2$, the feed was diluted with N$_2$, the space velocity was maintained high, and the reaction temperature was kept below 350 °C. However, hot spots might still appear in the bed and care must be taken when operating the catalysts under exothermic conditions. The performance of Cu/ZnO based catalysts during extended on-stream operation was investigated in the SRM reaction at 250 °C. This temperature is the highest temperature such that the production of CO is not favored. The results are shown in Figure 6.

The catalyst stability test over Cu/ZnO/Al$_2$O$_3$ catalyst was carried in the same tubular reactor used for the catalyst activity test. Figure 6 shows the results of methanol conversion in the stability test for 36 h. The catalyst stability test was carried out at WHSV 0.75 h^{-1}. The catalyst exhibited 80-82 % of methanol at the initial stage for 17 hours. It can be observed that the stable activity was obtained in the range of 0 – 17 hours. After 17 hours of stability test, the

reaction condition was changed in order to observe the catalyst response to the condition changes. At this point, the WHSV was changed to 4 h^{-1}. It is clearly observed that the methanol conversion was decreased to 60-62%, and this conversion remained constant for 12 hours of stability test. In this condition, the concentration of hydrogen in product gas was > 52%. The catalyst stability test results suggested that metallic Cu phase was well dispersed on the Al$_2$O$_3$.
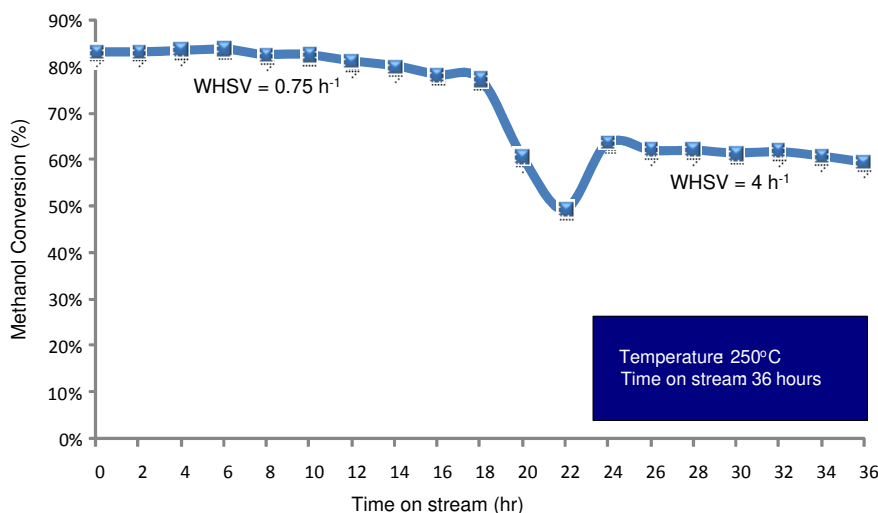

Figure 7 The catalyst stability measured at 250 °C for 36 hours of reaction.

4 Conclusions

Production of H$_2$ from methanol by steam reforming was studied over Cu/ZnO-based catalysts. The catalysts were prepared by the impregnation of Cu and Zn nitrates solution in γ-Al$_2$O$_3$. Numerous activity tests were carried out in order to investigate the influence of various parameters, such as feed flow rate and reaction temperature.

The catalyst shows a good activity and stability. A high conversion of methanol can be easily obtained by decreasing the space velocity of methanol. At 300 °C, the methanol conversion reached 100% at WHSV 0.75 h^{-1}. The conversion was decreased with the increasing of WHSV. At this temperature, the selectivity of hydrogen was 100% since there was no methanol condensation products detected. However, the production of CO was observed at 275 °C and 300 °C, although at very small concentration. The selectivity of CO$_2$ at these reaction

temperatures were 97% and 94% respectively, indicating that the $Cu/ZnO/Al_2O_3$ is a selective catalyst of steam reforming of methanol for hydrogen production.

The $Cu/ZnO/Al_2O_3$ exhibited a good stability at 250 °C for 36 hours of time on stream. The methanol conversion was maintained constant at about 80-82% in the first 12 hours period of stability test using WHSV of 0.75 hr^{-1}. The catalyst performance was still stable after the WHSV was changed to 4 hr^{-1}. At this condition, the methanol conversion was maintained stable at 60-62% for 12 additional hours.

Acknowledgement

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