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Research Article

Modification the Oxalic Co-precipitation Method on a Novel Catalyst $Cu/Zn/Al_2O_3/Cr_2O_3$ for Autothermal Reforming Reaction of Methanol

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Abstract

This study addresses the catalytic performance of $Cu/ZnO/Al_2O_3/Cr_2O_3$ in low-temperature of autothermal reforming (ATR) reaction. Various operating conditions were used to decide the optimum reaction conditions: type of promoter (ZrO_2, CeO_2, and Cr_2O_3), precipitation temperature, precipitation pH, operation temperature, molar ratio of O_2/CH_3OH (O/C), and weight hourly space velocity (WHSV). The catalysts were prepared using the oxalic coprecipitation method. Characterization of the catalyst was conducted using a porosity analyzer, XRD, and SEM. The methanol conversion and volumetric percentage of hydrogen using the best catalyst ($Cu/ZnO/Al_2O_3/Cr_2O_3$) exceeded 93% and 43%, respectively. A catalyst prepared by precipitation at -5 °C and at pH of 1 converted methanol to 40% H_2 and less than 3000 ppm CO at reaction temperature of 200 °C. The size and dispersion of copper and the degradation rate and turnover frequency of the catalyst was also calculated. Deactivation of the Cu catalyst at a reaction temperature of 200 °C occurred after 30 h. © 2013 BCREC UNDIP. All rights reserved

Keywords: hydrogen production; reaction kinetics; steam reforming; turnover frequency

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1. Introduction

The world's growing population has a significant effect on the demand for energy. To date, fossil fuels have served as the main energy sources to meet this demand. Unfortunately, fossil fuel will likely be depleted after 50-100 years [1]. A looming energy shortage is thus becoming an important problem for humankind, prompting a worldwide search for alternative energy sources [1,2]. The recent global energy shortage and more stringent emission regulations have stimulated research and development in fuel cells [3]. Hydrogen fuel cells seem to be a promising solution to these global environmental and energy problems. This is because using hydrogen fuel cell produces useful energy at high efficiencies, with heat and water being the only emissions [4].

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Methanol is a suitable liquid fuel for producing hydrogen because it has a high hydrogen-carbon ratio, is easy to handle, and has a reforming temperature [5-7]. Methanol reforming is an endothermic reaction that runs rapidly at temperature of 250-300 °C using copper-based catalysts [8]. Cu/ZnO catalysts, with their high selectively and activity, produces hydrogen through the steam reforming of methanol with high selectivity and activity [9,10]. High-activity catalysts are in high demand for on-board mobile applications in which the catalyst must be active, even at low temperatures during cold start-up.

Reitz and co-workers [11] reported that the catalytic performance of a Cu/Zn/Al catalyst depends greatly on the copper oxidation state (Cu^0, Cu^+, and Cu^{2+}). Cu/ZnO catalysts achieve their highest activity at higher temperatures, but their performance is inadequate at lower temperature reforming, which is more favorable to fuel cell processes [11,12]. Wu and co-workers [13] reported that autothermal reforming reaction could be performed at a lower temperature of 240 ^oC, and showed that the methanol conversion and CO volumetric percentage was more than 95% and less than 1%, respectively. CO concentration increases with the temperature because the methanol degradation rate ($CH_3OH \rightarrow CO + 2\ H_2$) at high temperature is more sensitive than the rate of the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) [13]. Some catalysts may exhibit higher activity in lower temperature reforming, but the decomposition reaction of methanol occurs simultaneously, forming a significant amount of CO. Conversely, Huang and coworkers [14] added oxygen to the steam-reforming methanol reaction over Cu/ZnO and $Cu/ZnO/Al_2O_3$ catalysts, demonstrating that 30–40 wt% Cu was the most active value for partial oxidation and steam reforming methanol reactions. However, the effects of any metal species on catalyst activity, remains unclear [14].

This research aims at modifying the catalyst preparation techniques (our oxalic co-precipitation method) so that the characteristics of the catalyst can be changed so that the catalyst can be used on low temperature reaction and carbon monoxide produced little. This study also describes the effects of using ZrO^{2-}, CeO^{2-}, and $Cr_2O_3^-$ promoted $Cu/Zn/Al_2O_3$ catalysts, precipitation temperature and pH, operation temperature, O/C molar ratio and WHSV on catalytic performance. The catalysts were prepared by oxalic co-precipitation. The reaction parameters included a precipitation temperature ranging from -5 to 25 ^oC, precipitation pH ranging from 1 to 9, operation temperature of 180 to 260 ^oC, O/C molar ratio of 0.23 to 0.45, WHSV of 6.22 to 11.50 h^{-1}, and ZrO^{2-}, CeO^{2-}, and $Cr_2O_3^-$ promoted catalysts.

2. Experimental

2.1. Materials

Methanol (99%, Mallinckrodt, American), copper nitrate-2.5-hydrate (99%, R.D.H, Germany), zinc nitrate-6-hydrate (99%, R.D.H, Germany), chromium nitrate-6-hydrate (99%, R.D.H, Germany), cerium nitrate-6-hydrate (99%, R.D.H, Germany), zirconium nitrate-6-hydrate (99%, R.D.H, Germany)acetone (99%, J.T. Baker, American), aluminum nitrate-9-hydrate (99%, J.T. Baker, American), oxalic acid (99%, R.D.H, Germany), and other reagents are all expanded chemicals.

2.2 Preparation of $Cu/ZnO/Al_2O_3/Cr_2O_3$ catalyst

Known quantities of $Cu(NO_3)_2.2.5H_2O$, $Zn(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$ and $Cr(NO_3)_2.6H_2O$ were introduced into a 100-cm^3 ethanol solution to form a concentration of 1 $kmol/m^3$ in a flask, and then stirred until well dissolved at a selected temperature of -5 to 25 ^oC. The solution was reacted with 20% excess oxalic acid of 0.5 $kmol/m^3$. The mixture was mixed with an ammonia solution (about 25% NH_3) until reaching a selected pH of 1 to 9 as measured using a pH meter (SP-701, Suntex, Taiwan). The precipitate was subsequently filtered and washed with deionized water, and then dried at 120 ^oC for 18 h. All precursors were calcined with the programmed temperature method in N_2 (100 cm^3/min) as given in Scheme 1.

After calcinations, the catalyst was ground into granules, and 60-80 mesh catalytic particles were sieved out. The catalyst was then reduced with a stream of 10% H_2/N_2 (100 cm^3/min) at a temperature of 25 ^oC to 300 ^oC with a heating rate of 5 ^oC /min for 3 h in ambient atmosphere. The catalyst properties were characterized using a porosity analyzer (Micromeritics ASAP2020, American) to determine the BET surface, size of pore, and volume

$$\text{RT} \xrightarrow{\text{30min}} 150\ ^oC \xrightarrow{\text{25min}} 150\ ^oC \xrightarrow{\text{20min}} 200\ ^oC \xrightarrow{\text{25min}} 200\ ^oC$$

$$\xrightarrow{\text{20min}} 250\ ^oC \xrightarrow{\text{25min}} 250\ ^oC \xrightarrow{\text{20min}} 300\ ^oC \xrightarrow{\text{3h}} 300\ ^oC$$

Scheme 1. The programmed temperature method of calcinations in N_2 (100 cm^3/min)

of pore. X-ray diffractometer (Shimadzu Labx XRD-6000, Japan) with Cu-Ka radiation (0.15418 nm) was used to determine the crystal size and dispersion of Cu on the catalyst. A crystallite size of Cu was estimated based on the Scherrer relation, L= 0.9.θ/βcosθ, where L is the crystallite size, θ is the wavelength of radiation, β is the broadening of the peak caused by small crystallites (rad 2θ), and θ is the corresponding angle of the diffraction peak. The full width at half maximum (FWHM) of Cu (1 1 1) was estimated at 43°. The correction for instrumental broadening was neglected because the FWHM of each refined peak was five times more than the instrumental broadening. The preparation of other types of the catalysts with a designated promoter (CeO_2, Cr_2O_3 or ZrO_2) was identical to this procedure.

2.3 Catalyst Activity Measurement

The experimental apparatus used in this study was reported in our previous work [13]. First, the catalysts, prepared as showed in Section 2.2, were placed in a U-shaped quartz tube measuring 1 cm in diameter and 15 cm in length. The tube was then placed in an electrically heated furnace. The temperature was controlled by a microprocessor-based temperature controller through a K-type thermocouple. The reaction temperature was measured at outlet of catalytic bed. The catalytic bed contained about 0.2 g of 60-80 mesh catalyst particles. Silicon carbide was placed between the entrance of the reactive tube and the top of the catalytic bed.

The mixture of methanol and water, which had a molar ratio of 1.2, was introduced to an evaporator through a syringe pump (Cole Parmer, 79400 series, American) at a rate of 2.4 cm^3/h. Air flow to an evaporator with 20 standard cubic centimeters per minute (sccm). This mixture (water, methanol and air) was then heated to evaporate to the gas phase after passing through an evaporator. All runs were conducted at an atmospheric pressure and at a selected temperature of 180 to 260 °C. The outlet of the reactor was also heated with electric heating tape to prevent condensation of the compounds in the gas.

The mixture gas was carried to a catalytic bed by 20 standard cubic centimeters per minute (sccm) air flow, and the WHSV operated at a selected value ranging from 6.22 to 11.50 h^{-1}. Methanol and water were condensed in a condenser with isopropanol of 100 mL. The liquid was collected to determine the methanol content using a gas chromatograph (Shimadzu 14B, Japan) with a flame ionization detector (FID), carrier gas of nitrogen as a mobile phase (30 cm^3/min), the mixture hydrogen gas (0.9 kg/cm^2) and air (0.6 kg/cm^2) as a detector. Column is 7HK-G013-22 ZB-WAX, Length 30 m, I.D. 0.53 mm, film 1 µm and temperature ranges from 45 to 75 °C. The sample was withdrawn at a selected time interval of 1 h.

The concentrations of H_2, CO, and CO_2 were measured using a gas chromatograph (Shimadzu 8A, Japan) with a thermal conductivity detector (TCD), a carrier gas of helium as a Mobile phase with flow 30 cm^3/min, a molecular sieve 13X column, a Chromosorb 120 column, and temperature range of 100 to 160 °C. The sample was withdrawn at selected time interval of 1 h.

2.4 Mathematical Equation for Measuring Catalyst Activity

The final compounds of this autothermal reforming reaction process were methanol (M), water (H_2O), hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). Other byproducts were not detected in this work. Thus, X_M and S_{CO2} in Eqs (1) and (2) respectively denote the methanol conversion and selectivity of carbon dioxide. In Eqs (3) and (4), V_{H2} and V_{CO} denotes the concentration of hydrogen and carbon monoxide, respectively.

$$X_M(\%) = \frac{C_{M,0} - C_{M,unreacted}}{C_{M,0}} \text{ x } 100 \qquad (1)$$

$$S_{CO_2}(\%) = \frac{C_{CO_2}}{C_{CO} + C_{CO_2}} \text{ x } 100 \qquad (2)$$

$$V_{H_2}(\%) = \frac{C_{H_2}}{C_{total}} \text{ x } 100 \qquad (3)$$

$$V_{CO}\,(ppm) = \frac{C_{CO}}{C_{total}} x\ 10^6 \qquad (4)$$

The term $C_{i,o}$ denotes the initial concentration of i chemicals (kmol/m^3) as measured by a gas chromatograph. The production rate per weight of the catalyst R_{H2} and molar flow rate F_{H2} of hydrogen can then be expressed as:

$$r_{H_2} = \frac{F_{H_2}}{\text{weight of catalyst}} \qquad (5)$$

and

$$F_{H_2} = (3 - \alpha).F_{CH_3OH}.X_{CH_3OH}, 0 \le \alpha \le 1 \qquad (6)$$

where α denote ratio of oxygen flow rate to methanol flow rate. Eqs. (7) and (8) show the activity A_{CU} and the turnover frequency (TOF), respectively.

$$A_{Cu} = \frac{F_{CH_3OH}X_{CH_3OH}}{\text{weight of catalyst}} \qquad (7)$$

$$\mathrm{TOF} = \frac{A_{Cu}}{3600\,\frac{sec}{h}.1000\,\frac{mmol}{mol}}.\frac{63.5\,\frac{g}{molCu}}{D} = 1.76 \times 10^{-5}\,\frac{A_{Cu}}{D} \qquad (8)$$

where the dispersion (D) of Cu content on the catalyst using the calculated XRD is shown as:

$$D(\%) = \frac{2 \cdot Cu(surface)}{Cu(Total)} x100\% \qquad (9)$$

Assume that copper is the face-centered cubic (fcc) structure with an average area of (100), (110), and (111) placed in 0.0711 nm^2 = 1.4 x 10^{19} Cu atom/m^2Cu, one get an equation of specific copper surface area:

$$S_{Cu} = \frac{Cu.N_{av}}{Cu(total) \cdot M_{Cu} \cdot 1.4 \times 10^{19}} \approx 1353\,\frac{Cu(surface)}{Cu(total)}\left(\frac{m^2Cu}{gCu}\right) \approx 677D\left(\frac{m^2Cu}{gCu}\right) \qquad (10)$$

where: N_{av} and M_{Cu} are 6.02 x 10^{23} atom/mol and 63.5 g/mol, respectively.

3. Results and Discussion

Our previous work [13] shows that the catalytic performance of autothermal reforming reaction using a $Cu/ZnO/Al_2O_3$ (CZA) mol ratio of 15:15:5 can obtain high catalytic activity using the combinatorial chemistry method at a reaction temperature of 240 °C. This study used this catalyst composition in the following analysis.

3.1 Modification of precipitation temperature on oxalic co-precipitation method

Zhang and co-workers [15] showed that the stripping-precipitation approach can be explored to control particle agglomeration and size [15], hence; this study investigates the precipitation temperature of the catalyst. The $Cu/ZnO/Al_2O_3$ (CZA) catalysts were prepared with different precipitation temperatures of 25, 15, 10, -5, and -10 °C.

Table 1 shows a Cu particle size of CZA of approximately 10.7 nm at -5 °C, which is smaller than those of other catalysts. Kawamura and co-workers [16] showed that the high dispersion of Cu is the result of the small crystallite size in the precipitate because of slow formation at a low temperature [16]. The current results support this finding, showing that the formation of a small crystal through optimization of the precipitation condition is effective for preparing $Cu/ZnO/Al_2O_3$ catalysts with high catalytic activity.

This study was analyzes Cu catalysts using SEM to investigate their surface morphology and XRD for phase identification of a crystalline material of Cu catalysts at different precipitation temperature. SEM images of $Cu/Zn/Al_2O_3$ catalyst are presented in Figure 1 and XRD was shown in Figure 2. From Figure 1, it appears that the lower temperature precipitation then pore texture on the surface of the catalyst is spread more evenly and clumping does not occur, so that the surface area of the catalyst becomes increasingly large. This is in accordance with the XRD data in Figure 2, where precipitation is low temperature (-5 °C), the maximum peak for Cu was very low, it can be interpreted that Cu was distributed evenly on the catalyst.

From Figure 2, the peak intensity was apparently decreased from CZA_25°C to CZA_-5°C with decreasing temperature, and the major diffraction peak of Cu were observed at 2θ angles of 43.3°, 50.4°, 74.1°. The agglomeration of catalysts apparently decreased when the precipitation temperature of the catalyst gradually decreased from CZA_25 °C to CZA_-5 °C. The dispersion of CZA_-5 °C is better than in other catalysts because Cu dispersion is affected by the amount of agglomeration. The particle shapes were uniformly distributed on all catalyst surfaces as the precipitation temperature of the catalyst gradually decreased. This distribution can be attributed to the small crystallite size in the precipitate caused by slow formation at a low temperature. This lower temperature was beneficial to the formation of micro crystallites, and not favorable to the growth of particles. The

Table 1 Cu particle size and BET surface area of the catalysts at different precipitation temperatures

Catalysts	FWHM[a] (degree)	Cu crystal size (nm)	D[b] from XRD (%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
CZA_25 °C	0.67	12.8	8.1	50.2	0.199	15.9
CZA_15 °C	0.7	12.3	8.5	63.7	0.41	26
CZA_10 °C	0.72	11.4	9.1	68.1	0.43	24.7
CZA_-5 °C	0.8	10.7	9.7	67.4	0.49	29.06

[a]: FWHM: Full Width at Half Maximum

[b]: D: dispersion of Cu on the catalyst

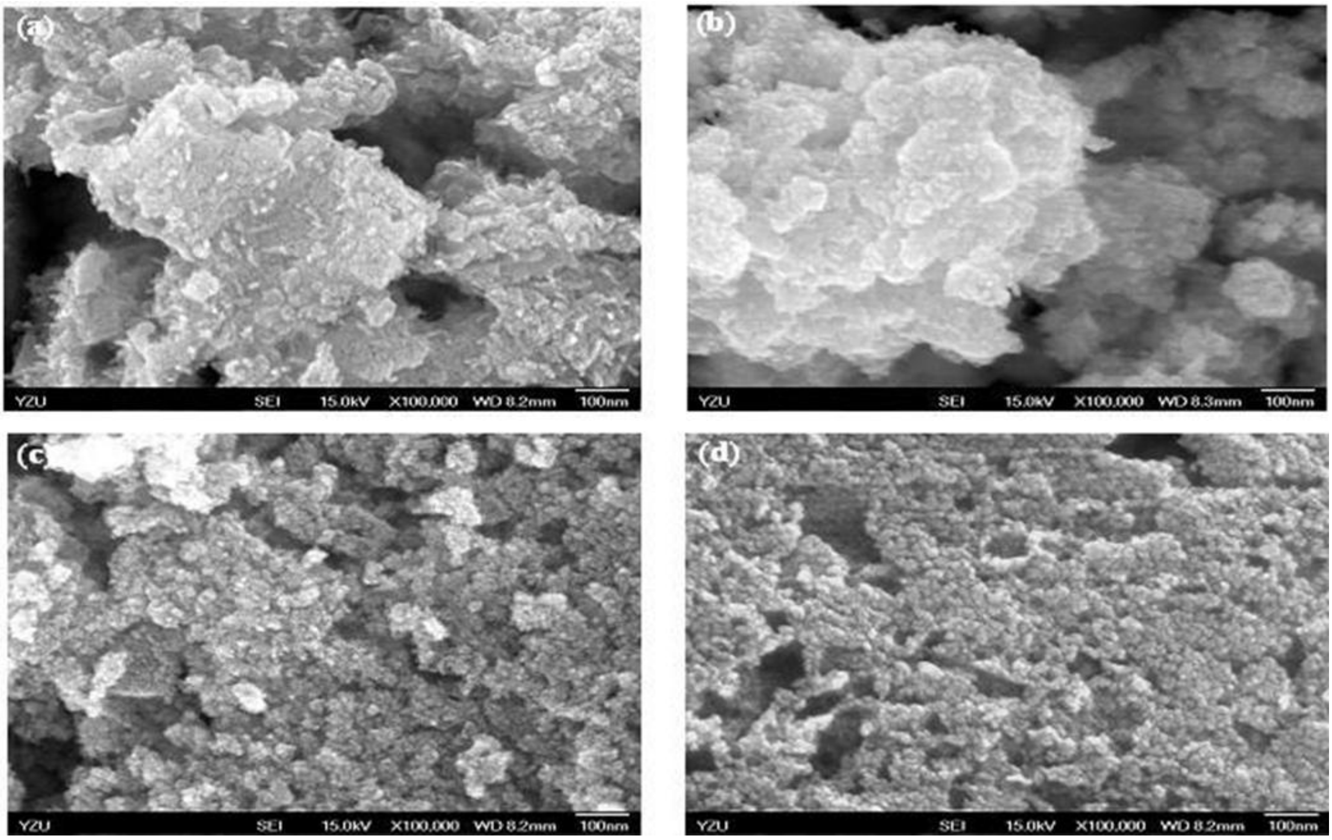

Figure 1. SEM photographs of the CZA catalyst in 100000-X (a) CZA _ 25 °C (b) CZA_15 °C (c) CZA_10 °C (d) CZA_-5 °C

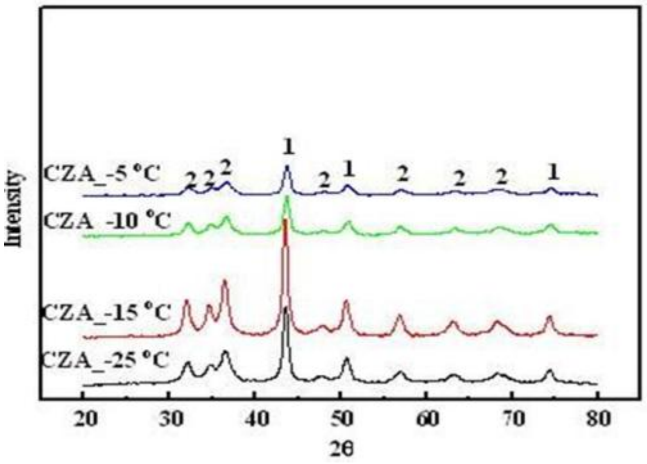

Figure 2. XRD intensity showing the effect of precipitation temperature on the CZA catalyst (1) Cu, (2) ZnO

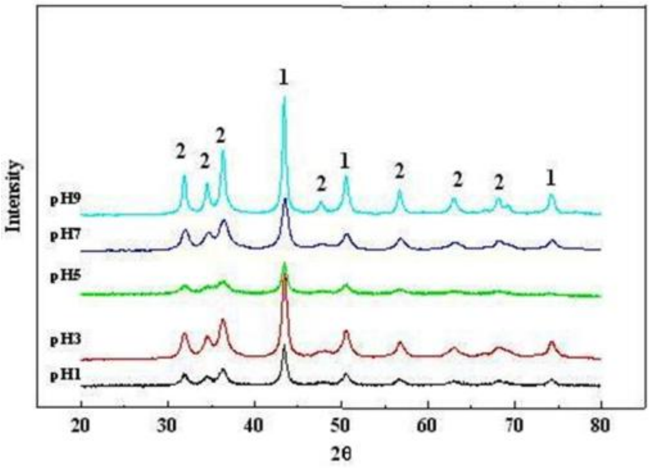

Figure 3. XRD intensity showing the effect of pH on the CZA catalyst (1) Cu, (2) ZnO

mass transfer rate increased and the viscosity of the solution decreased with increasing temperature [15]. Hence, a precipitation temperature of -5 °C was the best temperature for the precipitation catalyst in this study.

3.2 Effect of Various pH on Oxalic Co-precipitation Method

Figure 3 shows XRD diffractograms of Cu catalysts at different pH values in the H_2-reduced state, highlighting the characteristic peaks of Cu and ZnO. The major diffraction peak of Cu appeared at 2θ angles of 43.3°, 50.4°, and 74.1°. Table 2 shows crystallite sizes of the Cu and BET surface

Table 2. Cu particle size and BET surface area of the catalysts at various pH values

Catalysts	FWHM (degree)	Cu crystal size (nm)	D from XRD (%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	pore size (nm)
CZA-pH1	0.62	13.8	7.5	70.78	0.371	17.9
CZA-pH3	0.64	13.42	7.7	45.7	0.283	21.3
CZA-pH5	0.7	12.26	8.5	76.5	0.311	16.3
CZA-pH7	0.78	10.7	9.7	67.4	0.49	16.4
CZA-pH9	0.49	17.58	5.9	32.36	0.184	22.7

area of the catalyst. The particle size of Cu ranged from 13.8 to 17.6 nm for different pH values. In Table 2, Cu particle size decreases as the pH increase until pH=7, after this value, the particle size increases. The particle size increased in conjunction with the pH value. This phenomenon has been reported by Kawamura et al. [7].

Kawamura and co-workers [16] discussed the effect of pH on the Cu catalyst in methanol reforming. They predicted an excess of Cu species existing as amorphous-like malachite in the precursor [16]. Kawamura and co-workers [16] reported that Cu^{2+} in precipitates transforms into malachite through anion exchange with copper hydroxycarbonate ($Cu_2 (OH)_{4-2x} (CO_3)_x$), which replaces part of the OH^- in amorphous Cu $(OH)_2$ with CO_3. When precipitation was conducted at a high pH, the high concentration of OH^- in the solution suppressed the replacement of OH^{--} in $Cu(OH)_2$, preventing its transformation to malachite.[16] Therefore in our results, the catalyst which prepared by oxalic co-precipitation method in high pH value was low activities.

Experimental results show that the sequence of methanol conversion for the $Cu/ZnO/Al_2O_3$ catalyst is CZA-pH1 > CZA-pH5 > CZA-pH3 > CZA-pH7 > CZA-pH9, and the CO concentration was kept between 1000 ppm and 4000 ppm when the reaction temperature was 200 °C. These results show that CZA-pH1 is the best catalyst for methanol reforming.

3.3 Effect of WHSV

Space velocity is also a crucial factor that can influence the catalyst activity and concentration profiles. The hydrogen production rate is directly proportional to the WHSV of methanol [7]. It's because in catalytic reaction process, converting reactant gas into product needs many steps to be completed. Reactant gases transport into catalyst through gas-solid interface, and finally take a part in the surface reaction. Diffusion of reactant gas is often influenced by gas velocity, and surface reactions are generally influenced by contacting time of reactant species with catalysts. Increase in space velocity will increase gas velocity and promote mass transfer but decrease the contacting time. As a results, concentration of CO and H_2 conversion decrease linearly with space velocity increasing [17].

Figure 4 shows, the methanol conversion and concentration of CO decreased when the WHSV increased. This occurs since the higher the WHSV then lower the residence time of the reactants in the catalytic bed. The volumetric percentage of hydrogen production for 240 °C exceeded 40%. Hence, the WHSV was set at 7.27 h^{-1} because the methanol conversions and concentration of carbon monoxide were less than 90% and 3000 ppm, respectively. The turnover frequency increases with the WHSV, with a maximal approximately value of 0.18 s^{-1}. At a constant WHSV, CO concentration increased with temperature increasing. The effects of temperature and WHSV on H_2 conversion were similar to those on CO conversion, as shown in Figure 4, but H_2 conversion was lower than the corresponding CO conversion due to water-gas shift reaction [17].

3.4 Effect of O/C molar ratio

The oxidation steam-reforming methanol reaction involves both partial oxidation methanol (POM) and steam-reforming methanol (SRM) reaction, so the concentration of O_2 should have a strong influence on catalytic performance [18]. The addition of oxygen to the feed mixture (oxidative methanol steam reforming) helps reduce catalyst deactivation because oxygen reduces or even suppresses coke formation [19]. Figure 5 shows the effects of a O/C molar ratio of 0.23 to 0.45 on autothermal reforming reaction at a reaction temperature ranging from 180 to 240 °C. The best O/C ratio in Figure 5 is 0.28, with a methanol conversion of 92%, volumetric percentage of hydrogen of 47.7%, and a CO concentration of 3000 ppm at a reaction temperature of 200 °C.

From Figure 5, the methanol conversion increases in conjunction with the O/C ratio. This finding shows that the introduction of O_2 can enhance the activity of the catalyst. According to the

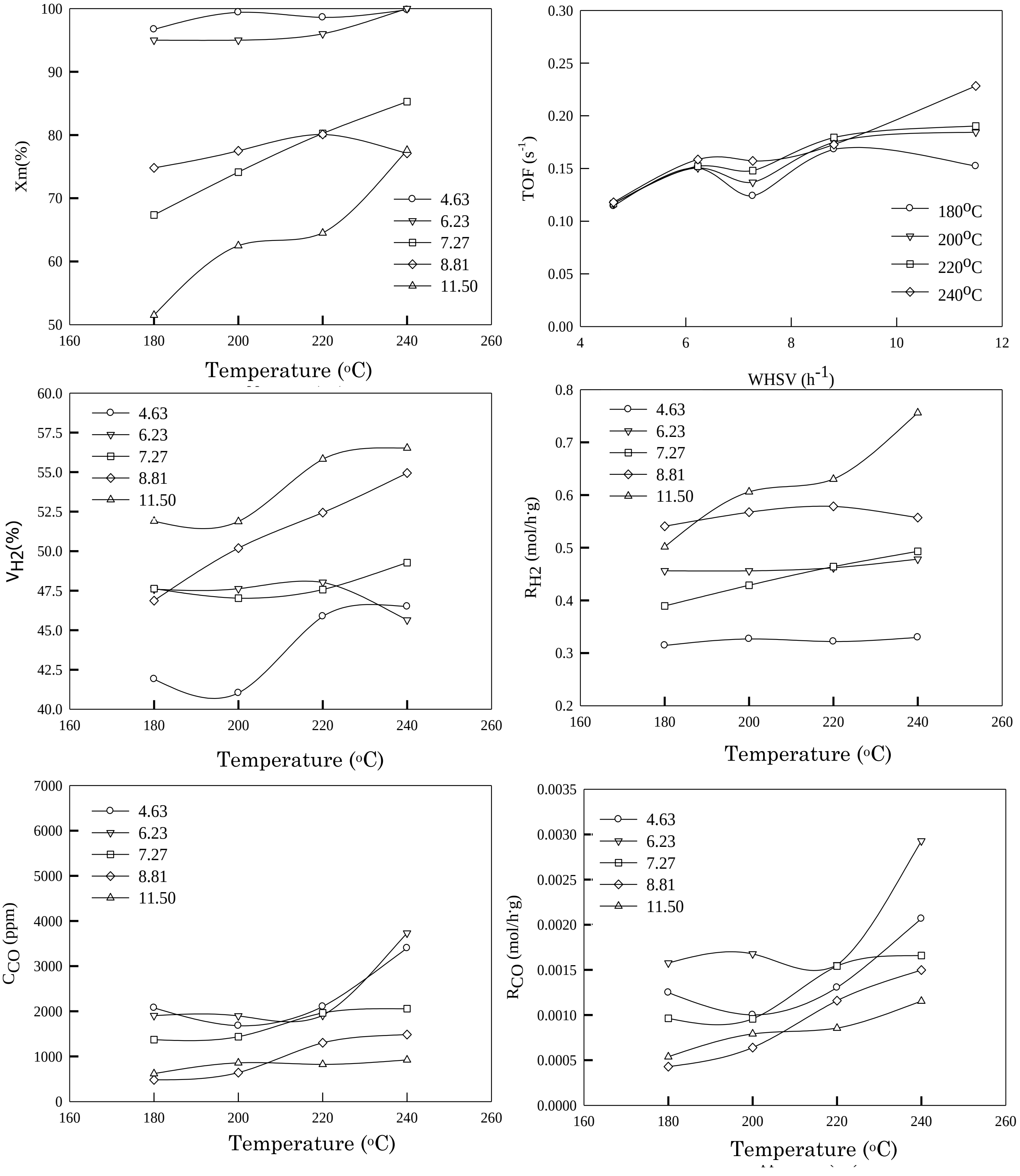

Figure 4. Effect of WHSV on autothermal reforming reaction. Catalyst: CZA_-5 °C, Catalyst weight = 0.2 g, O/C = 0.23, W/M = 1.2, WHSV = 6.22-11.50 h^{-1}, Temperature = 180-240 °C; X_m = methanol conversion; V_{H2} = hydrogen volume; C_{CO} = carbon monoxide concentration; TOF = Turnover frequency; R_{H2} = rate of hydrogen production; R_{CO} = rate of carbon monoxide production

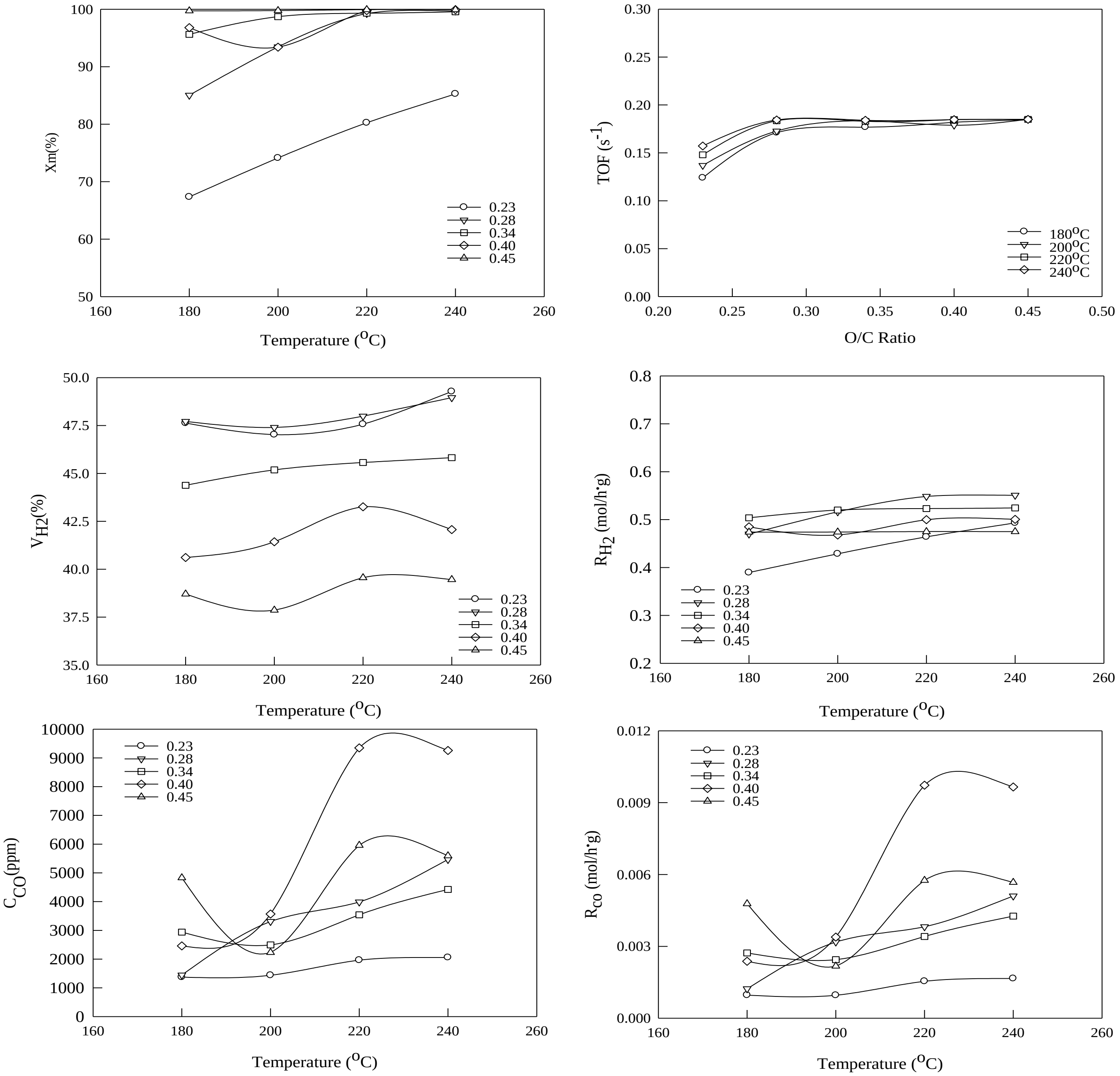

Figure 5. Effect of O/C ratio on autothermal reforming reaction. Catalyst: CZA_-5 °C, Catalyst weight = 0.2 g, WHSV = 7.23 h^{-1}, W/M = 1.2, O/C= 0.23-0.45, Temperature = 180-240 °C; X_m = methanol conversion; V_{H2} = hydrogen volume; C_{CO} = carbon monoxide concentration; TOF = Turnover frequency; R_{H2} = rate of hydrogen production; Rco = rate of carbon monoxide production

Table 3. Cu particle size and BET surface area for different composited catalysts (CZX)

Catalysts[a]	FWHM (degree)	Cu crystal size (nm)	D from XRD (%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	X_m at 30 h (%)
Cu(15)ZnO(15)Al_2O_3(5)	0.62	13.8	7.5	70.78	0.371	17.9	78.8
Cu(15)ZnO(15)ZrO_2(5)	0.6	14.3	7.3	40.01	0.24	24	80.6
Cu(15)ZnO(15)CeO_2(5)	0.53	16.2	6.4	36.7	0.2	21.5	56
Cu(15)ZnO(15)Cr_2O_3(5)	0.66	13	8.0	35.8	0.35	39.1	67

[a]: The value in the parenthesis is mol ratio.

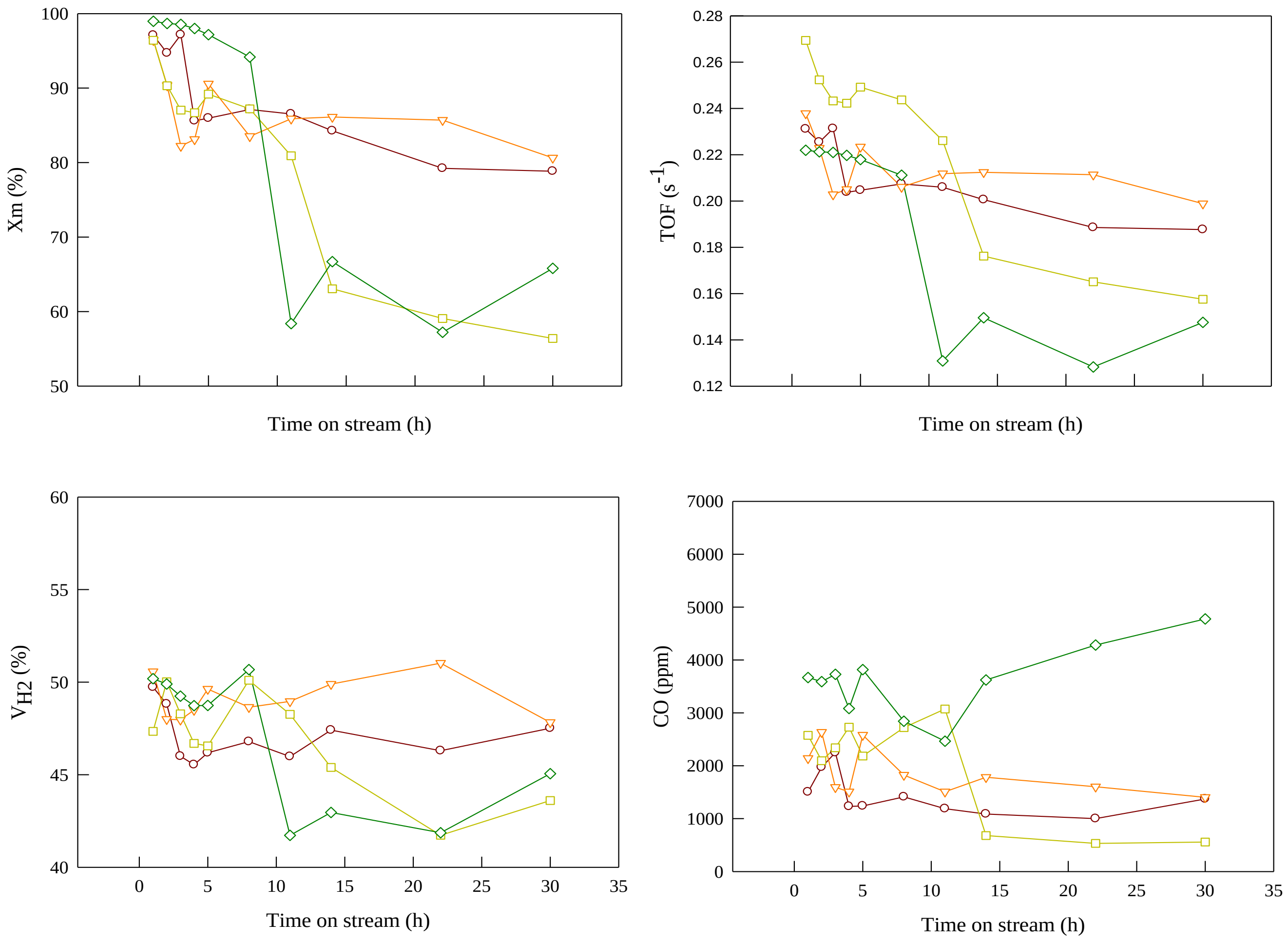

Figure 6. Life times of catalyst $Cu_{15}Zn_{15}X_5$ in autothermal reforming reaction. Catalyst weight = 0.2 g, WHSV = 7.27 h^{-1}, W/M = 1.2, O/C = 0.28, Temperature = 200 ^oC. (○) $Cu_{15}Zn_{15}Al_5$, (▽) $Cu_{15}Zn_{15}Zr_5$, (□) $Cu_{15}Zn_{15}Ce_5$, (◇) $Cu_{15}Zn_{15}Cr_5$; X_m = methanol conversion; V_{H2} = hydrogen volume; C_{CO} = carbon monoxide concentration; TOF = Turnover frequency

report by Wang and co-workers [20], a higher O/C ratio raised the concentration of CO. The highly exothermic reaction of methanol partial oxidation enhances the methanol decomposition reaction. Thus, CO selectivity is high when the O/C ratio in the feed is close to the stoichiometry of methanol partial oxidation [20].

3.5. Effect of Added Promoted Catalyst into Cu/ZnO Catalyst

The Cu–Zn–Al-oxide catalysts face the great problem of deactivation [21]. Saa and co-workers [19] showed that catalyst deactivation was related to the space velocity, and reported coke formation and active phase sintering [19]. Promoters need to add on a catalyst to solve the problem. Promoters have been used to influence the status of copper and enhance catalyst performance [18]. ZrO_2 support may improve the dispersion of Cu particles and stability in the catalyst [22]. Al_2O_3 support may improve the surface area of copper and thermal stability in the catalyst [23].

The Cu-Zn-X catalysts were prepared from Cu/Zn mixed with X: Al_2O_3, ZrO_2, CeO_2, or Cr_2O_3 before the reaction. Figure 6 shows the deactivation of Cu catalysts, methanol conversion, and H_2 and CO concentrations for 30 h on stream at a reaction temperature of 200 °C. The Cu-Zn-X catalysts were prepared from Cu/Zn mixed with Al_2O_3, ZrO_2, CeO_2, or Cr_2O_3 before the reaction. Promoters play an essential role in varying the physical and chemical properties of Cu/ZnO-based catalysts. Table 3 shows the BET surface area, and dispersion (D). The sequence of methanol conversion after a reaction time of 30 h is $Cu_{15}Zn_{15}Zr_5$ > $Cu_{15}Zn_{15}Al_5$ > $Cu_{15}Zn_{15}Ce_5$ > $Cu_{15}Zn_{15}Cr_5$.

3.6. Effect of Various Mol Ratio on Cu/ZnO/ Al_2O_3/Cr_2O_3 Catalyst

Figure 7 shows the comparison of the performance of Cu(15)ZnO(15)Al_2O_3(5) and Cu(15)ZnO(15) Al_2O_3(4)Cr_2O_3(1). Figure 7 shows that addition of the Cr_2O_3-promoter can increase the methanol conversion of the CZA catalyst by 5%. Similarly, a comparison of the Cu(15)ZnO(15)Al_2O_3(4)Cr_2O_3(1), Cu(15)ZnO(15)Al_2O_3(2.5)Cr_2O_3(2.5), and Cu(15)ZnO(15)Al_2O_3(1)Cr_2O_3(4) catalysts shows that the Cu(15)ZnO(15)Al_2O_3(2.5)Cr_2O_3(2.5) catalyst has the best reactivity. However, the CZA was added with too more the Cr_2O_3-promoter that CO concentration will be enhanced.

To find effect of mol ratio of catalyst into surface morphology, the catalyst was characterized by XRD and SEM. The XRD technique was also used to characterize the CZA and CZACr catalysts after autothermal reforming reaction. SEM was used to investigate surface morphology of catalyst. SEM images of Cu/Zn/Al_2O_3/Cr_2O_3 catalyst presented in Figure 8 and XRD patterns presented in Figure 9.

A comparison of the XRD patterns of Cu(15)ZnO(15)Al_2O_3(5) and Cu(15)ZnO(15)Al_2O_3(4) Cr_2O_3(1) catalysts shows that the addition of Cr_2O_3 can also improve the dispersion of Cu crystallites, leading to more active sites in catalysts. However, adding more Cr_2O_3-promoters to the CZA can lead to agglomeration. Thus, these results show that the Cr_2O_3-promoter can effectively improve the reaction activity and stability of the CZA catalyst, reducing the agglomeration of the CZA.

From Figure 8, it appears that added Cr_2O_3 on catalyst then pore texture on the surface of the catalyst is spread more evenly and clumping does not occur, so that the surface area of the catalyst becomes increasingly large. This is in accordance

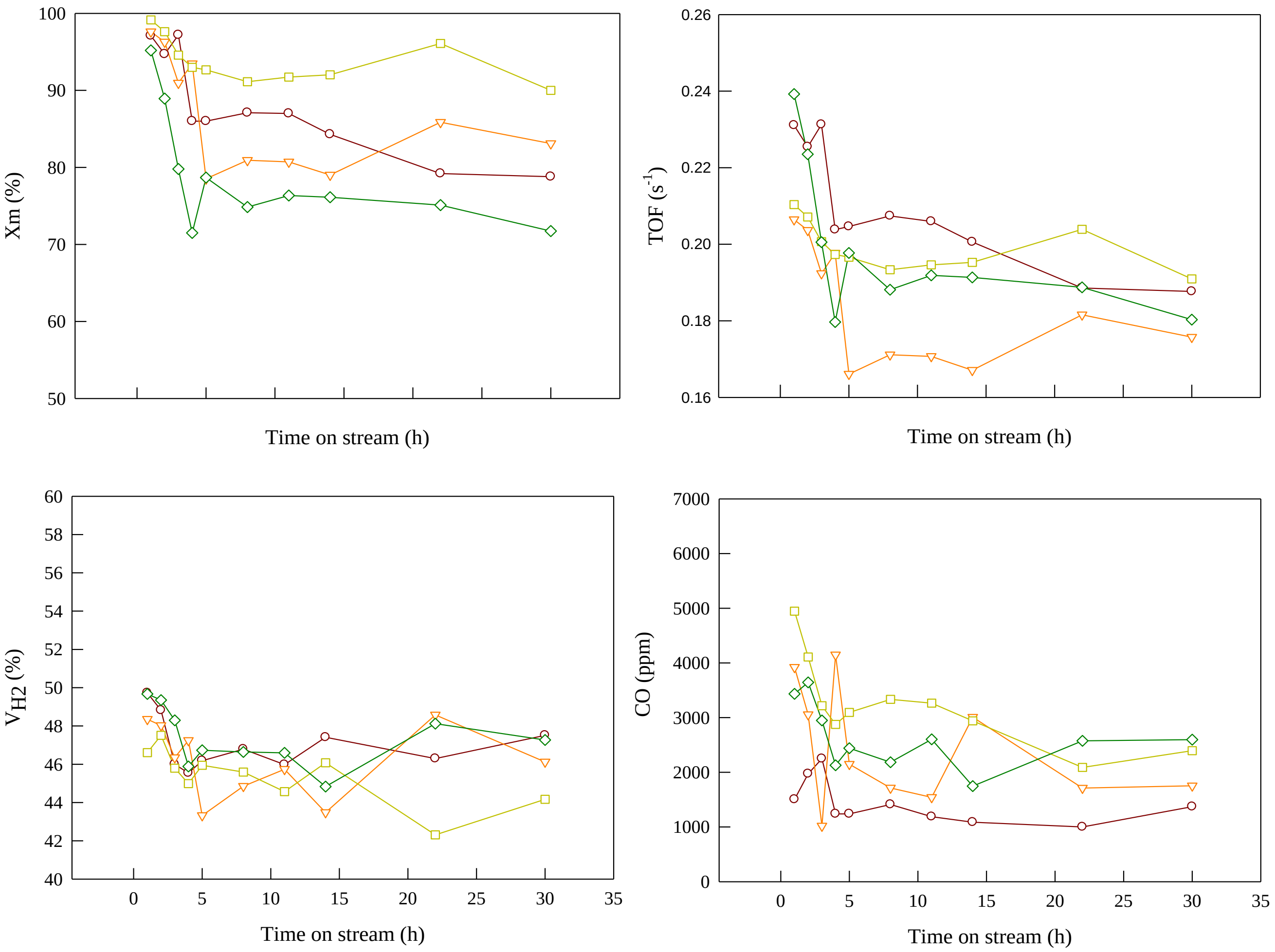

Figure 7. Effect of different mol ratio on Cu/ZnO/Al_2O_3/Cr_2O_3 catalyst. Catalyst weight = 0.2 g,WHSV = 7.27 h^{-1}, W/M = 1.2, O/C = 0.28, Temperature = 200 °C. precipitation pH = 1. (○) $Cu_{15}Zn_{15}Al_5$ (▽) $Cu_{15}Zn_{15}Al_4Cr_1$ (□) $Cu_{15}Zn_{15}Al_{2.5}Cr_{2.5}$, (◇) $Cu_{15}Zn_{15}Al_1Cr_4$; X_m = methanol conversion; V_{H2} = hydrogen volume; C_{CO} = carbon monoxide concentration; TOF = Turnover frequency

with the XRD data in Figure 9, where added Cr_2O_3, the maximum peak for Cu was very low, it can be interpreted that Cu was distributed evenly on the catalyst.

Table 4, has shown the Cu crystal size, FWHM was calculated by Debye-Scherer equation at the peak of Cu phase of 43.8o. From Table 4, Cu(15)Zn(15)Al_2O_3(2.5)Cr_2O_3(2.5) is higher crystal size. This result was linier with the results of catalyst activity in Figure 7. Higher crystal size can influence to higher catalyst activity.

3.7. Lifetime Services of Cu/ZnO/Al_2O_3/Cr_2O_3 Catalyst

Lifetime service of catalyst is important for commercializations of catalyst. Agarwal and coworkers [24] assumed that one major problem related to the operation of heterogeneous catalysis is the catalytic loss of activity with time on stream because of catalyst deactivation. One main cause of deactivation is the deposition of coke, which results from the formation of coke precursors such as carbon oxides and their subsequent decomposition [24]. An ideal catalyst can be used for a long time and has a lower deactivation.

To explain about catalyst deactivation in Cu(15)ZnO(15)Al_2O_3(2.5)Cr_2O_3(2.5) catalyst activity, this catalyst was used on ATR at reaction temperatures of 200 and 260 °C for 100 h (Figure 10). Figure 10, show that the Cu(15)ZnO(15)Al_2O_3(2.5) Cr_2O_3(2.5) catalyst has the good initial activity. However, the activity of the catalyst decreased slightly at first and then remained constant until 46 h. During this period, methanol conversion was approximately 91 and 92% for reaction temperatures of 200 and 260 °C, respectively, and then gradually decreased until 100 h with conversions of approximately 59 and 76%, respectively. The deac-

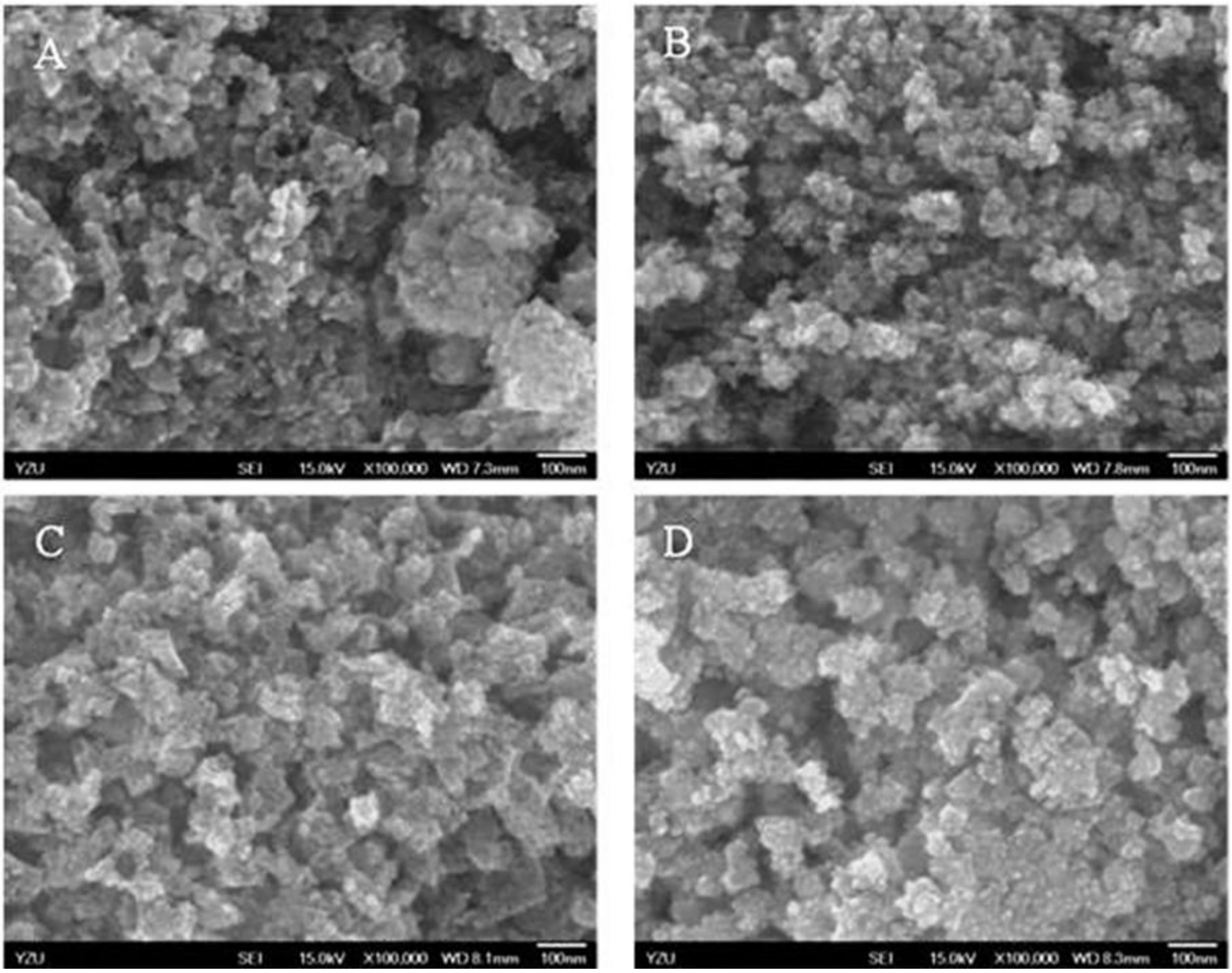

Figure 8. SEM photographs of different mol ratio of Cu/ZnO/Al_2O_3/Cr_2O_3 catalyst in 100000-X, (A) $Cu_{15}Zn_{15}Al_5$, (B) $Cu_{15}Zn_{15}Al_4Cr_1$, (C) $Cu_{15}Zn_{15}Al_{2.5}Cr_{2.5}$, (D) $Cu_{15}Zn_{15}Al_1Cr_4$

Table 4. Particle size and dispersion of Cu for different composited catalysts

Catalysts[a]	FWHM (degree)	Cu crystal size (nm)	D from XRD (%)
Cu(15)ZnO(15)Al_2O_3(5)	0.62	13.8	7.5
Cu(15)ZnO(15)Al_2O_3(4)Cr_2O_3(1)	0.7	12.26	8.5
Cu(15)ZnO(15)Al_2O_3(1)Cr_2O_3(4)	0.696	12.3	8.5
Cu(15)ZnO(15)Al_2O_3(2.5)Cr_2O_3(2.5)	0.59	14.57	7.1

[a]: The value in the parenthesis is mol ratio.

Table 5. Comparisons steam reforming methanol using Cu catalyst to produce hydrogen

Catalyst	Catalyst ratio	T_R (°C)	First conversion	Final conversion	Lifetimes (h)	References
Cu/ZnO/ZrO_2/Al_2O_3	12/5/5/78 [b]	260	90	88	20	[21]
Cu/ZnO/Al_2O_3		300	78	70	20	[24]
Cu/ZnO/ZrO_2/Al_2O_3	50/25/18.7/6.25[b]	260	97	93	5	[25]
Cu/ZrO_2	90/10[a]	260	90	28	7	[26]
Cu/Ce/Y/Zr/Cr/O+ Al_2O_3	0.2//0.5/0.2/0.1/0.1/y+ 40%	300	41	38	40	[27]
Cu/Cr/Mn/Si	75/18/4/3[a]	275	75	73	40	[28]
Cu/ZnO/Al_2O_3/Cr_2O_3	15/15/2.5/2.5[b]	200	99	91	40	This study
Cu/ZnO/Al_2O_3/Cr_2O_3	15/15/2.5/2.5[b]	260	99	93	40	This study

[a]: for weight ratio, [b]: for mol ratio

Table 6. Comparisons of catalytic performance

Catalyst	Ratio (wt%/*mol%*)	Temperature (°C)	Time on stream (h)	TOF[a] (s^{-1})	References
Cu/Zn/Al_2O_3	15/15/5	240	-	0.112	[13]
Cu/Ce-Zn	30/40-30	240	16	0.16	[29]
Cu/CeO_2	3.9	240	24	0.305	[30]
CuZnZrAl	15/15/10/60	250	-	0.175	[31]
Cu/Zn/Al_2O_3	15/15/5	240		0.18	This study
Cu/Zn/Al_2O_3/Cr_2O_3	15/15/4/1	200	100	0.123	This study
Cu/Zn/Al_2O_3/Cr_2O_3	15/15/2.5/2.5	260	100	0.162	This study

[a] Turnover frequency

tivation rate constants of Cu(15)ZnO(15)Al_2O_3(2.5) Cr_2O_3(2.5) are 0.66 h^{-1} (200 °C) and 0.33 h^{-1} (260 °C), respectively. This finding shows that the reaction temperature is a crucial factor in stabilizing the Cu catalyst during the reaction. Carbon deposited on the surface of a catalyst covers the copper sites, decreasing the number of sites available for methanol adsorption during the methanol steam-reforming reaction. [24]

Table 5 shows that the results in this study are better than those in previous researches. When the reaction temperature was 200 °C, the methanol conversion at the start of a reaction was extremely high (i.e.99%), and even after 40 h reaction, methanol conversion remained at 91%. Jeong et al. also obtained a high methanol conversion of 97% until 93% for the last reaction [25]. However, the reaction temperature was higher (260 °C) in that case,

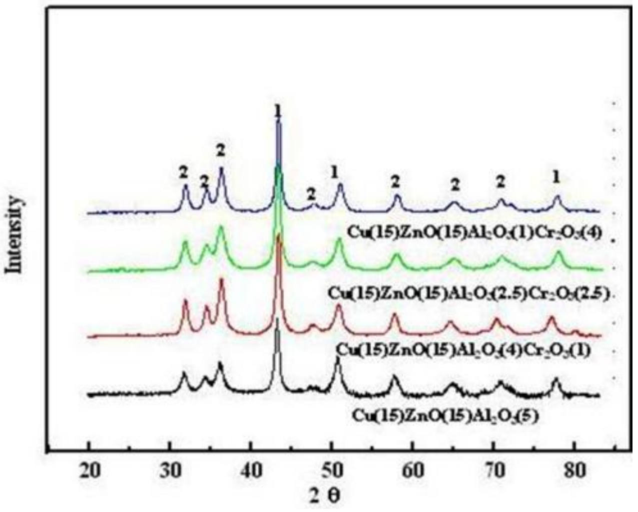

Figure 9. XRD intensity for the different mol ratio of Cu/ZnO/Al_2O_3/Cr_2O_3 catalysts (1) Cu, (2) ZnO

and the catalyst lifetime was 5 h. The lower temperature is needed for the reduction so that easier reducibility of the catalyst in the methanol reforming can lead higher activity. High dispersion and the large surface area of the catalyst can simplify the reduction. The Cu/Zn/Al_2O_3/Cr_2O_3 catalyst in this study has a lower deactivation rate and higher TOF than those in previous studies (Table 6).

5. Conclusions

The oxalic co-precipitation method preparative condition was controlled at a precipitation temperature of -5 °C and pH 1. Results show a methanol conversion of 93% and a volumetric percentage of hydrogen of 43%. The concentration of CO was smaller than 2000 ppm. The addition of a Cr_2O_3-promoter increased the stability of CZA; specifically, Cu(15)ZnO(15)Al_2O_3(2.5)Cr_2O_3(2.5) can re-

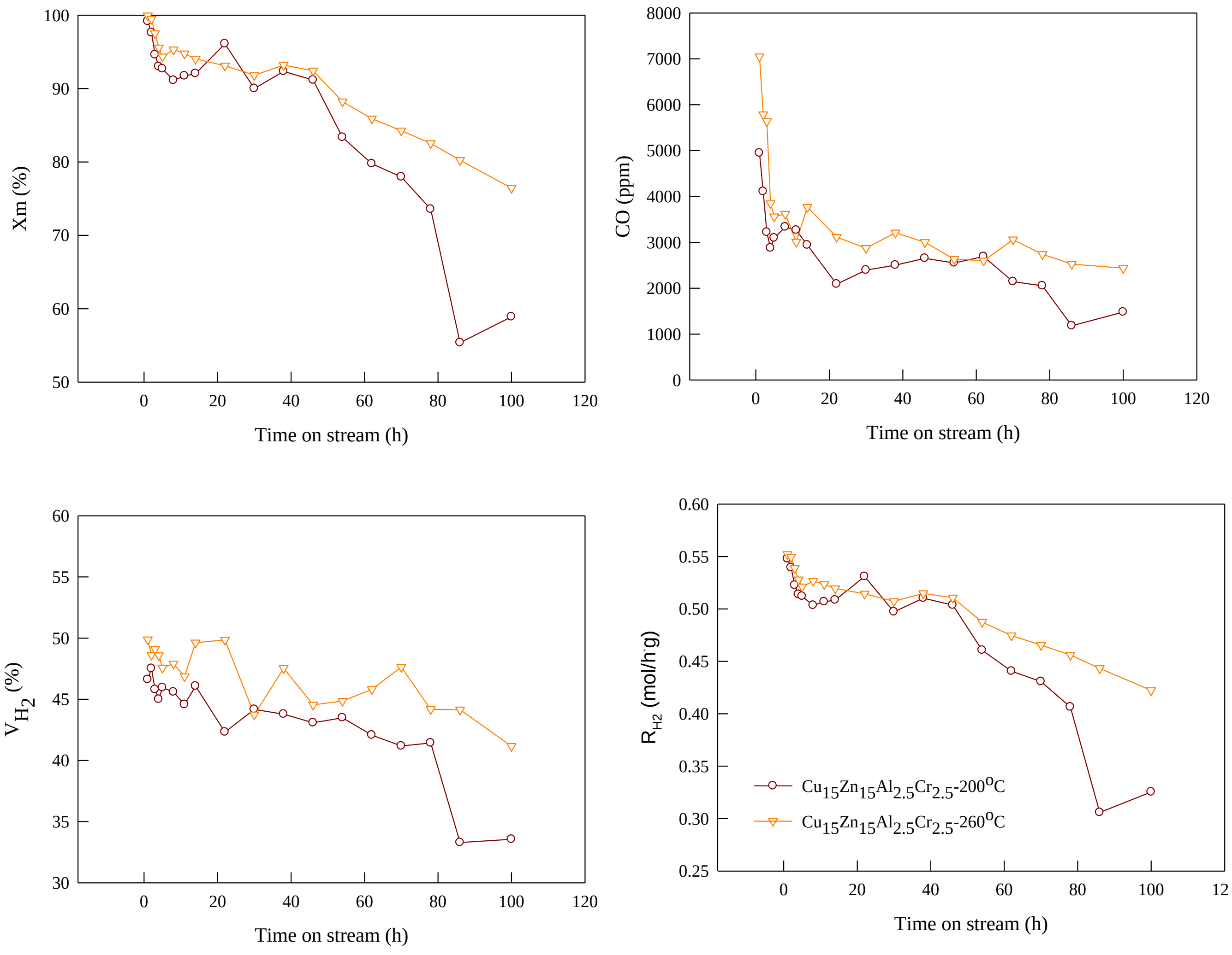

Figure 10. Lifetimes of catalyst $Cu_{15}Zn_{15}Al_{2.5}Cr_{2.5}$ in autothermal reforming reaction. Catalyst weight=0.2 g, WHSV= 7.27 h^{-1}, W/M= 1.2, O/C= 0.28, Temperature= (○) 200 °C and (▽) 260 °C; X_m = methanol conversion; V_{H2} = hydrogen volume; C_{CO} = carbon monoxide concentration; R_{H2} = rate of hydrogen production

sult in a methanol conversion of 92% at a reaction temperature of 200 °C for 46 h. These experimental results for methanol conversion were better than those reported in previous works. This study confirms that Cu/Zn derivatives can be conducted at a low temperature of less 200 °C, and last a long lifetime.

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References

[1] Suparoek, H., Toochinda, P. (2002). Effect of Preparation of Cu/Zn Over Al_2O_3 Catalyst for Hydrogen Production From Methanol Reforming. *Syranaree Journal Science Technology* 16: 103-112.

[2] Abdullah, M., Khairurrijal, K., Noor, F.A., Marully, A.R., Sanny, M. (2010). Design of Steam Reforming Reactor for Converting Methanol Into Hydrogen Using an Ultrasonic Nebulizer as Liquid Feeder and Polymer Liquid Processed $CuO/ZnO/Al_2O_3$ Particles as Catalyst. *Journal of Sustainable Energy and Environment* 1: 11-15.

[3] Chin, Y.H., Dagle, R., Hu, J., Dohnalkova, A.C., Wang, Y. (2002). Steam Reforming of Methanol over Highly Active Pd/ZnO Catalyst. *Catalysis Today* 77 : 79–88.

[4] Kruger, P. (2001). Electric Power Requirement for Large-Scale Production of Hydrogen Fuel for The World Vehicle Fleet. *International Journal of Hydrogen Energy* 26: 1137-1147.

[5] Geissler, K., Newson, E., Vogel, F., Truong, T.B., Hottinger, P., Wokaun, A. (2001). Autothermal Methanol Reforming for Hydrogen Production In Fuel Cell Applications. *Physical Chemistry Chemical Physics* 3: 289-293.

[6] Lindstrom, B., Pettersson, L.J. (2001). Hydrogen Generation by Steam Reforming of Methanol Over Copper-Based Catalysts for Fuel Cell Applications. *International Journal of Hydrogen Energy* 26: 923–933.

[7] Wu, H.S., Lesmana, D. (2012). Short Review: Cu Catalyst for Autothermal Reforming Methanol for Hydrogen Production. *Bulletin of Chemical Reaction Engineering & Catalysis* 7(1): 27-42.

[8] Ma, L., Jiang, C., Adesina, A.A, Trimm, D.L., Wainwright, M.S. (1996). Simulation Studies of Autothermal Reactor System for H_2 Production from Methanol Steam Reforming. *Chemical Engineering Journal* 62: 103-111.

[9] Mascaro´s, M.S., Navarro, R.M., Sainero, L.G., Costantino, U., Nocchetti, M., Fierro, J.L.G. (2001). Oxidative Methanol Reforming Reactions on CuZnAl Catalysts Derived from Hydrotalcite-like Precursors. *Journal of Catalysis* 198: 338-347.

[10] Navarro, R.M., Pena, M.A., Fierro, J.L.G. (2002). Production of Hydrogen by Partial Oxidation of Methanol over a $Cu/ZnO/Al_2O_3$ Catalyst: Influence of the Initial State of the Catalyst on the Start-Up Behaviour of the Reformer. *Journal of Catalysis* 201: 112-118.

[11] Reitz, T.L., Ahmed, S., Krumpelt, M. Kumar, R., Kung, H.H. (2000). Methanol Reforming Over CuO/ZnO Under Oxidizing Conditions. *Studies in Surface Science and Catalysis* 130: 3645-3650.

[12] Reitz, T.L., Lee, P.L., Czaplewski, K.F., Lang, J.C., Popp, K.E., Kung, H.H. (2001). Time-Resolved XANES Investigation of CuO/ZnO in the Oxidative Methanol Reforming Reaction. *Journal of Catalysis* 199: 193-201.

[13] Wu, H.S., Chung, S.C. (2007). Kinetics of Hydrogen Production of Methanol Reformation Using $Cu/ZnO/Al_2O_3$ Catalyst. *Journal of Combinatorial Chemistry* 9: 990-997.

[14] Huang, T.J., Wang, S.W. (1988). Kinetics of Partial Oxidation of Methanol Over a Copper—Zinc Catalyst. *Applied Catalysis* 40: 43-55.

[15] Zhang, D.X., Xu, H., Liao, Y.Z., Li, H.S., Yang, X.J. (2009). Synthesis and Characterisation of Nano-Composite Copper Oxalate Powders by a Surfactant-Free Stripping–Precipitation Process. *Powder Technology* 189: 404-408.

[16] Kawamura, Y., Yamamoto, K., Ogura, N., Katsumata, T., Igarashi, A. (2005). Preparation of $Cu/ZnO/Al_2O_3$ Catalyst for A Micro Methanol Reformer. *Journal of Power Sources* 150: 20-26.

[17] Guo, J.W., Niu, Y.Q., Zhang, B.J. (1998). Effect of Temperature and space velocity on catalytic performance in liquid phase dimethyl ether synthesis from syngas. *Journal*

of Natural Gas Chemistry 7: 259-265.

[18] Velu, S., Suzuki, K., Kapoor, M.P., Ohashi, F., Osaki, T. (2001). Selective Production of Hydrogen for Fuel Cells via Oxidative Steam Reforming of Methanol over CuZnAl(Zr)-Oxide Catalysts. *Applied Catalysis A: General* 213: 47-63.

[19] Saa, S., Silva, H., Brandãoa, L., Sousaa, J.M., Mendesa, A. (2010). Catalysts for Methanol Steam Reforming - a Review. *Applied Catalysis B: Environment* 99: 43-55.

[20] Wang, Z., Xi, J., Wang, W., Lu, G. (2003). Selective Production of Hydrogen by Partial Oxidation of Methanol Over Cu/Cr Catalysts. *Journal of Molecular Catalysis A: Chemical* 191: 123-134.

[21] Patel, S., Pant, K.K. (2006). Activity and Stability Enhancement of Copper–Alumina Catalysts Using Cerium and Zinc Promoters for The Selective Production of Hydrogen via Steam Reforming of Methanol. *Journal Power Sources* 159: 139-143.

[22] Matsumura, Y., Ishibe, H. (2009). High Temperature Steam Reforming of Methanol Over Cu/ZnO/ZrO_2 Catalysts. *Applied Catalysis B: Environment* 91: 524–532.

[23] Matsukata, M., Uemiya, S., Kikuchi, E. (1988). Copper-Alumina Spinel Catalysts For Steam Reforming of Methanol. *Chemical Letter*. (5): 761-764.

[24] Agarwal, V., Patel, S., Pant, K.K. (2005). H_2 Production by Steam Reforming of Methanol Over Cu/ZnO/Al_2O_3 Catalyst: Transient Deactivation Kinetics Modeling. *Applied Catalysis A: General* 279: 155-164.

[25] Jeong, H., Kim, K.I., Kim, T.H., Ko, C.H., Park, H.C., Song, I.K. (2006). Hydrogen Production by Steam Reforming of Methanol in a Micro-Channel Reactor Coated with Cu/ZnO/ZrO_2/Al_2O_3 Catalyst. *Journal Power Sources* 159: 1296–1299.

[26] Wu, G.S., Mao, D.S., Lu, G.Z., Cao, Y., Fan, K.N. (2009). The Role of the Promoters in Cu Based Catalysts for Methanol Steam Reforming. *Catalyst Letter* 130: 177–184.

[27] Yaseneva, P., Pavlova, S., Sadykoy, V., Moroz, E., Burgina, E., Dovlitova, L., Rogov, V., Badmaev, S., Belochapkin, S., Ross, J. (2008). Hydrogen Production by Steam Reforming of Methanol Over Cu–CeZrYOx-Based Catalysts. *Catalyst Today* 138: 175–182.

[28] Cheng, W.H. (1995). Reaction and XRD Studies on Cu Based Methanol Decomposition Catalysts: Role of Constituents and Development of High-Activity Multicomponent Catalysts. *Applied Catalysis A: General* 130: 13-30.

[29] Tsai, M.C., Wang, J.H., Shen, C.C., Yeh, C.T. (2011). Promotion of a Copper–Zinc Catalyst with Rare Earth for The Steam Reforming of Methanol at Low Temperatures. *Journal of Catalysis* 279: 241-245.

[30] Liu, Y., Hayakawa, T., Suzuki, K., Hamakawa, S., Tsunoda, T., Ishii, T., Kumagai, M. (2002). Highly Active Copper/Ceria Catalysts for Steam Reforming of Methanol. *Applied Catalysis A: General* 223: 137–145.

[31] Jones, S.D., Weaver, H.E.H. (2009). Steam Reforming of Methanol Over CeO_2- and ZrO_2-Promoted Cu-ZnO Catalysts Supported on Nanoparticle Al_2O_3. *Applied Catalysis B: Environment* 90: 195-204.