

Kinetics of Hydrogen Production of Methanol Reformation Using Cu/ZnO/Al₂O₃ Catalyst

Ho-Shing Wu* and Shun-Chang Chung

Department of Chemical Engineering and Materials Science, Yuan-Ze University, 135 Yuan Tung Road, ChungLi, Taoyuan, 32003, Taiwan

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The catalytic performance of methanol reformation using Cu/ZnO/Al₂O₃ was investigated at low temperature. The operation conditions, such as composition of Cu, Zn, and Al, temperature, molar ratio of H₂O/CH₃OH, weight hourly space velocity, catalyst weight, and kind and flow rate of carrier gas (helium and air), were evaluated to obtain the optimum reaction condition. The catalysts were prepared by oxalic coprecipitation, coprecipitation, and polyol method. The weight composition of Cu, Zn, and Al prepared by oxalic coprecipitation was 15:15:5 by high-throughput screening of combinatorial chemistry method, which was the best Cu/ZnO/Al₂O₃ catalyst. The prepared catalysts showed high activity and selectivity towards hydrogen formation. The methanol conversion, production rate, and volumetric percentage of hydrogen using this best catalyst were larger than 95%, 0.65 mol/h·g and 59%, respectively, and the CO volumetric percentage was smaller than 0.22% when the reaction temperature was 240 °C. The size and dispersity of copper, and the activity and turnover frequency of the catalyst were calculated as well.

1. Introduction

Fuel cells are a clean and efficient source of electrical power for both mobile and stationary applications. Hydrogen or hydrogen-rich feed gas is used as fuel in the fuel-cell system. Catalytic steam reforming is a widespread application. Methanol is a suitable liquid fuel for producing hydrogen because of its advantage of high hydrogen/carbon ratio, ease of handling, and low reforming temperature.^{1,2} Methanol reforming is an endothermic reaction that runs sufficiently fast at 250–300 °C on copper-based catalysts.³ Cu/ZnO catalyst can be used to produce hydrogen by steam reforming of methanol of high selectivity and activity.^{4,5} Reitz et al.^{6,7} reported that the catalytic performance of a Cu/Zn/Al catalyst was strongly dependent on the copper oxidation state, i.e., Cu⁰, Cu⁺, or Cu²⁺. Cu/ZnO catalyst is well known to show the highest activity at higher temperatures, but is insufficient for lower-temperature reforming which is more favorable to fuel cell processes. Moreover, some catalysts may exhibit higher activity at lower temperature reforming, but the decomposition reaction of methanol took place simultaneously to form significant amounts of CO. On the other hand, the addition of oxygen to the steam reforming methanol reaction over Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts was initially investigated by Huang and co-workers^{8,9} who demonstrated that 30–40 wt% Cu was the most active for the partial oxidation and steam reforming methanol reactions. However, it is still not clear how each metal species in each catalyst affects the catalyst activity.

This paper presents the results on the preparation and testing of a series of copper-containing catalysts for this reaction. The work aims to find the active catalysts for the reaction to operate at temperatures low enough that carbon monoxide is not a significant product. The purpose of this research is to investigate the effect of composition included in Cu/Zn/Al, temperature, ratio of H₂O/CH₃OH, weight hourly space velocity, catalyst weight, and kind and flow rate of carrier gas (helium and air) on methanol reformation. The catalysts were prepared by oxalic coprecipitation, coprecipitation, and polyol method. Besides, there were 27 different compositions of Cu, Zn, and Al prepared by oxalic coprecipitation to find the best Cu/ZnO/Al₂O₃ catalyst determined by H₂ production rate by high-throughput screening of combinatorial chemistry method. The parameters for temperature were 200–300 °C, feed composition of H₂O/CH₃OH ranged from 0.4 to 2.0, weight hourly space velocity was from 7.18 to 57.4 h⁻¹, catalyst weight was 0.1–0.5 g, flow rate of carrier gas ranged from 15 to 50 sccm, and tested carrier gases were air and helium. The properties of the catalysts were characterized by a porosity analyzer (Micromeritics ASAP2000) and X-ray diffractometer (Shimadzu Labx XRD-6000).

2. Experimental Section

2.1. Materials. Methanol (99%, Mallinkrodt, American), copper acetic-1-hydrate (99%, RDH, Germany) copper nitrate-2.5-hydrate (99%, RDH, Germany), zinc acetic-1-hydrate (99%, RDH, Germany), zinc nitrate-2.5-hydrate (99%, RDH, Germany), γ -aluminum oxide (99%, Osaka, Japan), oxalic acid (99%, RDH, Germany), and other reagents are all expanded chemicals.

* To whom correspondence should be addressed. Tel: (+886)-3-4638800-2564. Fax: (+886)-3-4559373. E-mail: cehsww@saturn.yzu.edu.tw.

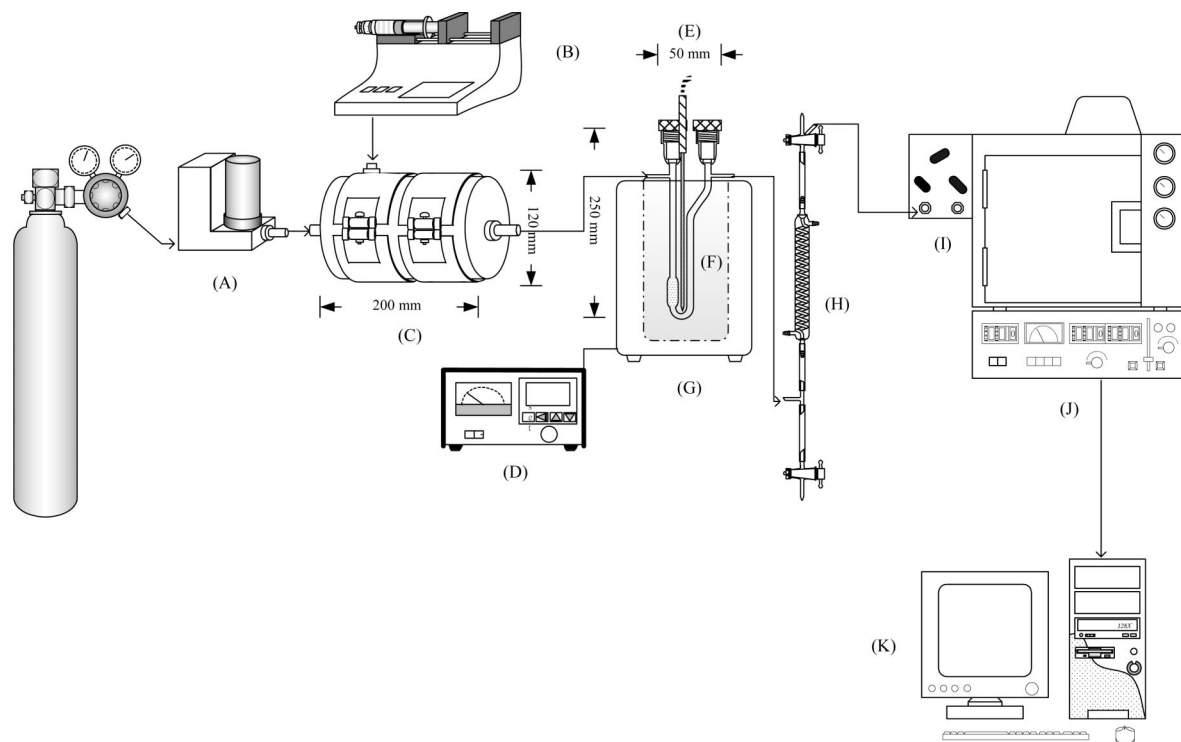


Figure 1. Schematic diagram of experimental apparatus: (A) flow controller, (B) syringe pump, (C) evaporator, (D) temperature controller, (E) thermocouple, (F) U-type gas-phase reactor, (G) fixed-bed reactor, (H) condenser, (I) gas sampler, (J) GC with TCD, (K) computer.

2.2. Synthesis of Cu/ZnO/Al₂O₃ Catalyst. **2.2.1. Preparation of Catalyst of Oxalic Coprecipitation Method.** Known quantities of Cu(NO₃)₂·2.5H₂O, Zn(NO₃)₂·6H₂O, and Al(NO₃)₃·9H₂O were introduced into a 100 cm³ ethanol solution to form a concentration of 1 kmol/m³ in a flask, and then stirred to well-dissolve at 25 °C. The solution was reacted with 20% excess oxalic acid of 0.5 kmol/m³. The mixture was mixed with ammonia solution (25 % NH₃) until a constant pH of 7 measured by pH meter. The precipitate was filtered, washed with water, and then dried 18 h at 120 °C.

2.2.2. Preparation of Catalyst by Coprecipitation Method. Known quantities of Cu(NO₃)₂·2.5H₂O, Zn(NO₃)₂·6H₂O, and Al(NO₃)₃·9H₂O were introduced into a 100 cm³ water solution to form a concentration of 1 kmol/m³ in a flask, and then stirred to well-dissolve at 25 °C. The mixture was mixed with 0.5 kmol/m³ Na₂CO₃ solution until a constant pH of 7 measured by pH meter. The precipitate was aged at 25 °C for 90 min with stirring, then filtered, washed with water, and dried 18 h at 120 °C.

2.2.3. Preparation of Catalyst by Polyol Method. Known quantities of Cu(CH₃COO)₂·H₂O and Zn(CH₃COO)₂·2H₂O were introduced into a 200 cm³ ethylene glycol solution to form a concentration of 1 kmol/m³ and stirred to well-dissolve at 25 °C. Four g of γ-Al₂O₃ support was added gradually into each solution of different molar ratios of Cu to Zn solution at 80 °C. After adding γ-Al₂O₃, the mixture was heated with refluxing temperature at 180 °C, and aged 10 min at 180 °C. The metal-glycol mixture was cooled to 25 °C, then filtered, washed with water and acetone alternately, and the precipitate was collected. The precipitate

was dried 18 h at 120 °C. All precursors were calcined by method of programmed temperature under N₂ (100 cm³/min).

After calcination, the catalyst was ground into granules and sieved out 60–80 mesh catalyst particles. Finally, the catalyst was reduced by stream of 10% H₂/N₂ (100 cm³/min) from 25 to 300 °C with a heating rate of 5 °C/min in atmosphere for 3 h.

2.3. Reaction Kinetics of Methanol Reformation. Figure 1 shows the diagram of the experimental apparatus. First, the catalysts prepared as indicated in Section 2.2 were put into a quartz tube of 1 cm diameter and 15 cm length. The tube was placed in an electrically heated furnace. The temperature was controlled by a microprocessor-based temperature controller through a thermocouple. The catalytic bed contained about 0.2 g of 60–80 mesh catalyst particles and was filled with silicon carbide between the entrance zone of the reactive tube and the top of the catalyst bed.

The mixture of methanol and water (molar ratio 1.2) was introduced into the evaporator by a syringe pump at 2.24 cm³/h, and heated to evaporate gas when passed through the evaporator. All runs were conducted at atmospheric pressure and at reaction temperature in the range of 200–300 °C. The reactive tube from the outlet of the reactor was also heated by electric-heating tape in order to avoid the compound in gas to be condensed. The gas compositions were measured by a gas chromatograph. The sample was withdrawn at selected time intervals of 1 h.

The mixture gas was carried to the catalytic bed by 50 sccm helium gas, the weight hourly space velocity was calculated equal to 14.4 h⁻¹. Methanol and water condensed

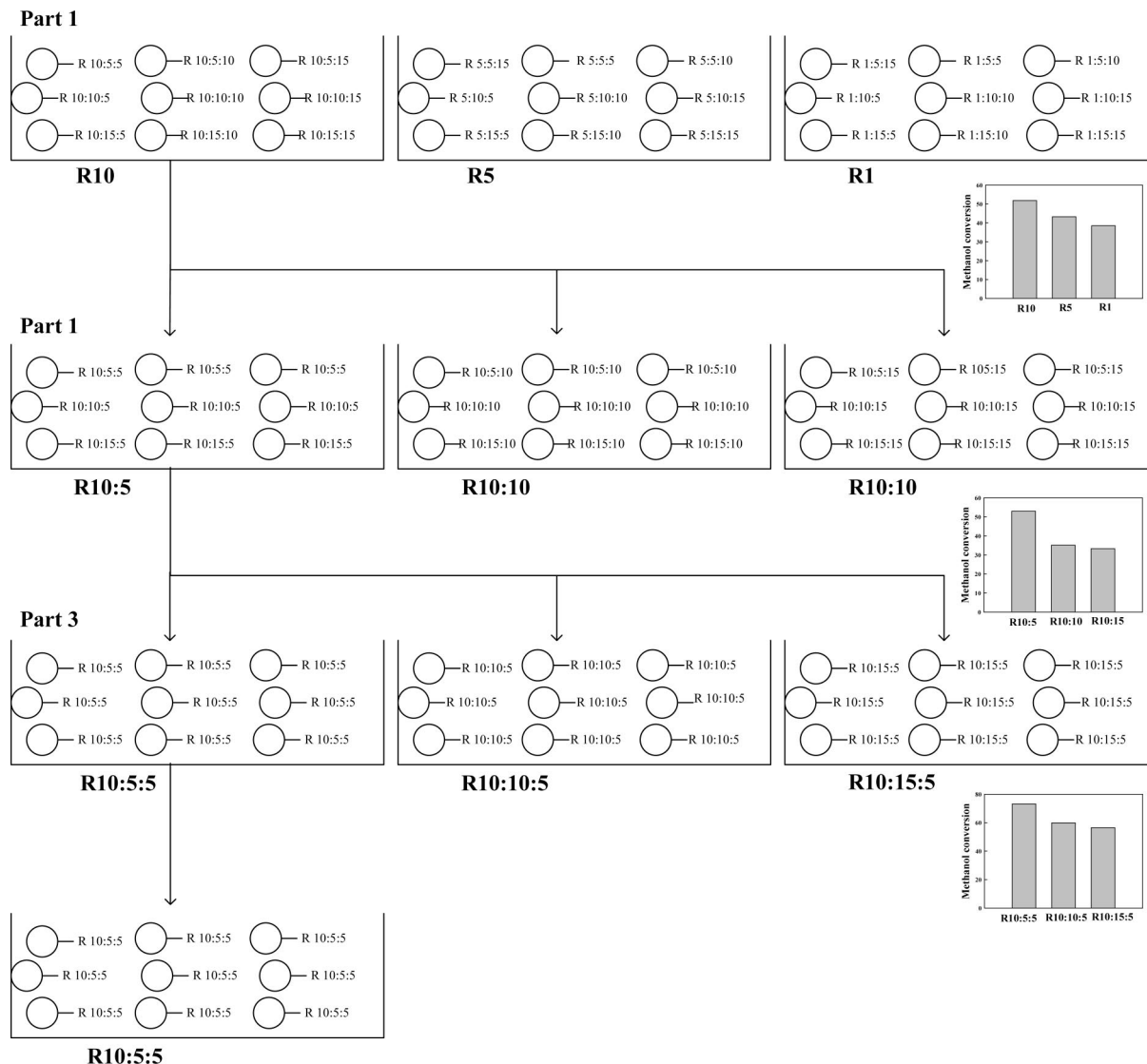


Figure 2. Schematic diagram of high-throughput screening.

Table 1. Methanol Conversion and CO₂ Selectivity of Cu/ZnO/Al₂O₃ on High-Throughput Screening for 240 and 300 °C

catalyst	240 °C		300 °C	
	X _M (%)	S _{CO₂} (%)	X _M (%)	S _{CO₂} (%)
R10	51.8	99.4	88.8	97.2
R5	43.2	97.5	78.0	91.0
R1	38.5	96.9	75.7	96.4
R10:5	53.0	98.1	98.6	95.2
R10:10	35.1	99.6	85.3	96.3
R10:15	33.3	99.6	83.4	97.8
R10:5:5	73.1	99.0	98.0	95.7
R10:10:5	59.9	98.9	97.0	92.3
R10:15:5	56.5	99.1	92.0	94.0

through the condenser and the liquid was collected to determine methanol by means of gas chromatograph (Shimadzu 14B, Japan) with flame ionization detector. The concentrations of H₂, CO, and CO₂ were measured by means of gas chromatograph (Shimadzu 8A, Japan) with thermal conductivity detector, with carrier gas of helium and with molecular sieve 13X column and chromosorb 120 column.

2.4. Mathematical Modeling. In this methanol reformation, the final compounds are methanol, H₂O, H₂, CO, and CO₂. The other byproduct was not detected in this work. Hence, X_M and S_{CO₂} calculated from eqs 1 and 2 denote the

methanol conversion and selectivity of carbon dioxide, respectively. V_{H₂} and V_{CO} denote hydrogen and carbon monoxide volumetric percentage, and are also given in eqs 3 and 4, respectively.

$$X_M = \frac{C_{M,0} - C_M}{C_{M,0}} \quad (1)$$

$$S_{CO_2} = \frac{C_{CO_2}}{C_{CO} + C_{CO_2}} \quad (2)$$

$$V_{H_2} = \frac{C_{H_2}}{C_{total}} \quad (3)$$

$$V_{CO} = \frac{C_{CO}}{C_{total}} \quad (4)$$

in which, C_i denotes the concentration of *i* chemicals (kmol/m³), measured by gas chromatograph. Then, the production rate per weight of the catalyst r_{H₂} and molar flow rate F_{H₂} of hydrogen was expressed as

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

and

$$F_{H_2} = F_M X_M (2 + S_{CO_2}) \quad (6)$$

The activity A_{Cu} and the turnover frequency (TOF) were calculated and are given in eqs 7 and 8.

$$A_{Cu} = \frac{X_M \cdot F_M}{\text{weight of catalyst}} \quad (7)$$

TOF =

$$\frac{A_{Cu}}{3600 \text{sec/h} \cdot 1000 \text{mmol/mol}} \cdot \frac{63.5 \text{g/mol Cu}}{\text{Cu content} \cdot \text{dispersion}} \quad (8)$$

3. Results and Discussion

3.1. Screening Cu/ZnO/ γ -Al₂O₃ Catalyst in Methanol Reformation. The Cu/ZnO/ γ -Al₂O₃ catalyst was synthesized with high-throughput screening of combinatorial chemistry.¹⁰ The synthesis of the catalyst was conducted by the mix-split method in this study. The mix-split method has the best efficiency for solid phase synthesis in the combinatorial chemistry. Steam reforming of methanol was chosen as the probing reaction. The detection was conducted by the iterative deconvolution method. The reactivity of the catalyst was influenced by particle size, composition of Cu, ZnO, and Al₂O₃, temperature, size and dispersion of Cu, and structure of active site. Because the composition of Cu, ZnO, and Al₂O₃ would directly affect the reactivity of the catalyst in the steam reforming reaction, this combinatorial library was made from composition of Cu, ZnO, and Al₂O₃. The three composition ratios of Cu, ZnO, and Al₂O₃ are 1, 5, and 10; 5, 10, and 15; and 5, 10, and 15, respectively. When the composition ratio of Cu, ZnO, and Al₂O₃ prepared by oxalic coprecipitation was 10, 5, and 5, respectively, the catalyst is named R10:5:5. Twenty-seven types of the catalyst were prepared in this study.

The iterative deconvolution method is usually used to screen out the most active catalysts from combinatorial

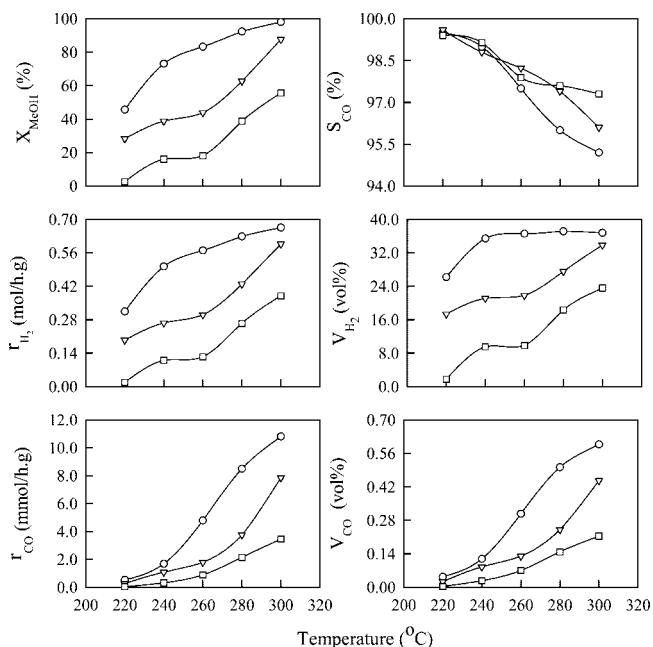


Figure 3. Effect of prepared method of catalyst on methanol reformation with different reaction temperatures. Catalyst = 0.2 g, He = 50 sccm, H₂O/CH₃OH = 1.2, WSHV = 14.4; four h⁻¹ (○) R10:5:5, (□) P10:5:5, (△) C10:5:5.

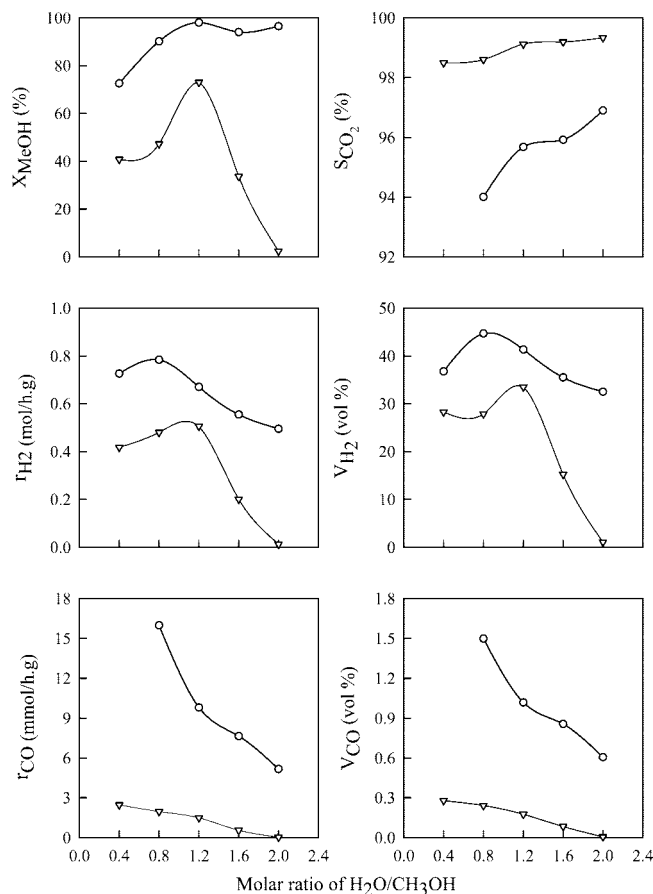


Figure 4. Effect of molar ratio of H₂O/CH₃OH on methanol reformation for 240 and 300 °C. Catalyst (R10:5:5) = 0.2 g, He = 50 sccm, WSHV = 14.4 h⁻¹; (○) 300 °C, (□) 240 °C.

libraries. Figure 2 shows the scheme of screening the library using the iteration deconvolution method. The probing reaction system chosen for this study was the reaction of methanol reforming. The reaction is given as



First, 27 kinds of catalysts as mentioned above were divided into three 9-membered sub-libraries of Cu (R10, R5, and R1). Each sub-library as the catalyst was conducted in the methanol reforming reaction. These reactions were conducted at 240 and 300 °C. The methanol conversion was in the following descending order: R10 > R5 > R1 (Table 1). Hence, the R10 catalysts were chosen as composition of Cu in the following screening procedure. The second screen was the screening of Cu and Al₂O₃ as shown in Figure 2. Nine kinds of catalysts were divided into three 3-membered sub-libraries (R10:5, R10:10, and R10:15). Each sub-library as the catalyst was conducted in the methanol reforming reaction. The methanol conversions were in the following descending order: R10:5 > R10:10 > R10:15. Hence, the R10:5 catalysts were chosen as composition ratio of Cu and Al₂O₃ in the following screening procedure. The final screening was the screening of ZnO as shown in Figure 2. Three kinds of catalysts were divided into three 1-membered sub-libraries (R10:5:5, R10:10:5, and R10:15:5). Each sub-library as the catalyst was conducted in the methanol reforming reaction. The methanol conversions

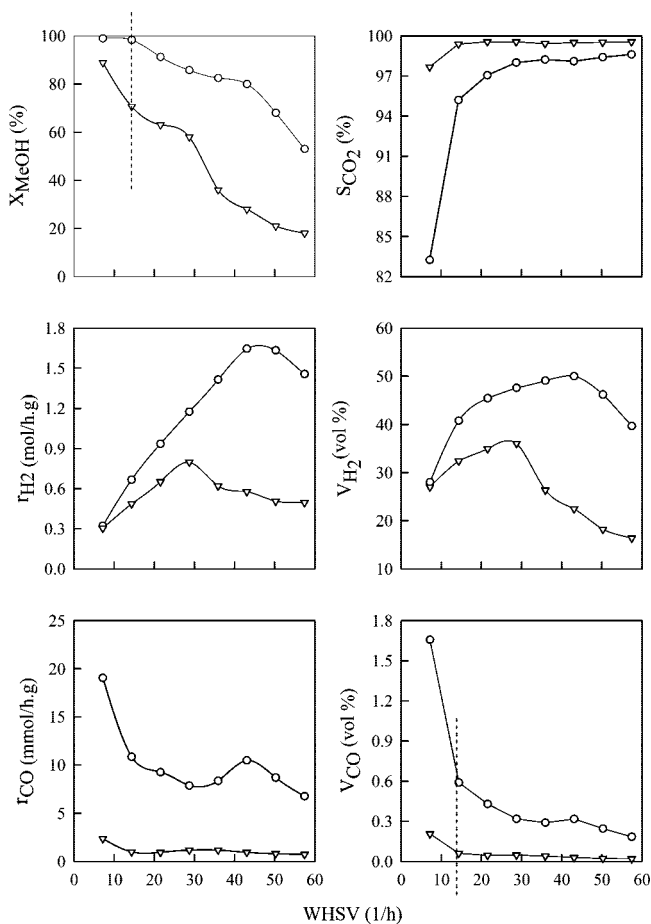


Figure 5. Effect of WHSV on methanol reformation. Catalyst (R10:5:5) = 0.2 g, He = 50 sccm, H₂O/CH₃OH = 1.2; (○) 300 °C, (◻) 240 °C.

were in the following descending order: R10:5:5 > R10:10:5 > R10:15:5. Therefore, the optimum composition ratio of Cu, ZnO, and Al₂O₃ was obtained as R10:5:5 in this screening. The conversion of methanol and the selectivity of CO₂ using R10:5:5 catalysts at 240 and 300 °C were 73.1% and 99.0%, and 98.0% and 95.7%, respectively.

3.2. Effect of Preparation Method of the Catalyst. The Cu/ZnO/ γ -Al₂O₃ catalysts were prepared by three methods of oxalic coprecipitation (R), coprecipitation (C), and polyol method (P). The methanol conversion was increased with a temperature rise no matter which method was used for preparation of the catalyst. The sequence of methanol conversion for catalytic preparation method was oxalic coprecipitation > polyol method > coprecipitation as shown in Figure 3. According to analysis of XRD spectrum, the Cu sizes calculated for oxalic coprecipitation, polyol method, and coprecipitation were 17.5, 36.5, and 65.7 nm, respectively. This means that the smaller Cu size resulted in the higher dispersion of Cu on the catalyst so that the methanol conversion was high. This result corresponds to the results of Lindstrom et al.¹¹ and Severino and Laine.¹²

The trend for hydrogen production rate is identical to the methanol conversion for different preparation methods. The production rate and the volumetric percentage of hydrogen for R10:5:5 during the range of 220 to 300 °C were in the range of 0.30 to 0.68 mol/h · g catalyst, and 0.25% to 0.38%, respectively. The methanol reformation is composed of the

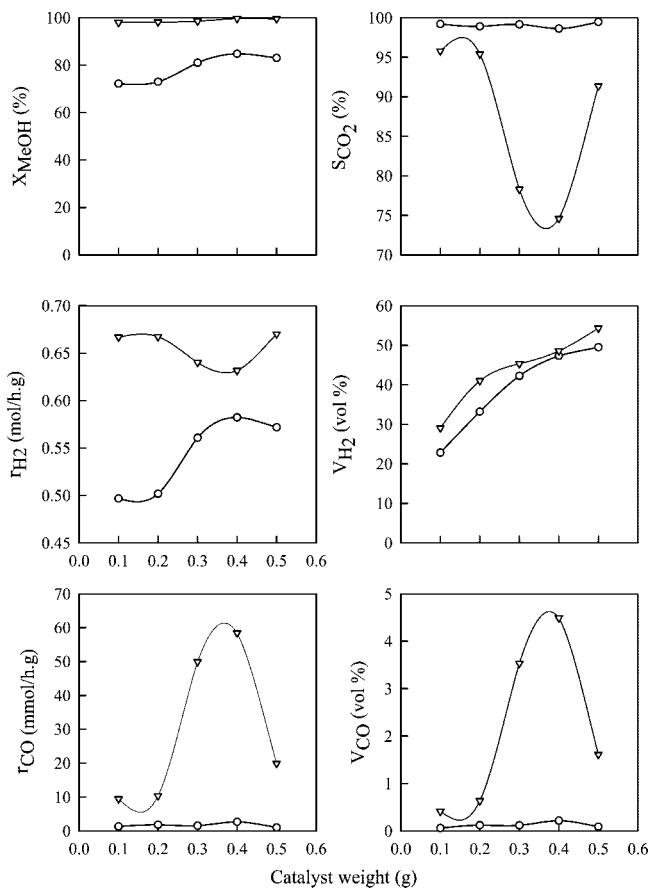


Figure 6. Effect of catalyst weight on methanol reformation. Catalyst: R10:5:5, WHSV = 14.4 h⁻¹, He = 50 sccm, H₂O/CH₃OH = 1.2; (◻) 300 °C, (○) 240 °C.

methanol degradation reaction (CH₃OH → CO + 2 H₂) and water-gas shift reaction (CO + H₂O → CO₂ + H₂). The CO concentration was increased with increasing the temperature because the methanol degradation rate for temperature was more sensitive than the water-gas shift reaction rate. According to the result shown in Figure 3, the CO concentration observed was influenced by two reactions at different temperatures. Therefore, two temperatures of 240 °C (lower) and 300 °C (higher) were chosen to study the operation parameter in order to achieve an optimum condition. We hope to find the best catalyst in this methanol reforming for lower temperature.

3.3. Effect of Molar Ratio of H₂O to CH₃OH in Influent. Figure 4 shows the effect of molar ratio of H₂O/CH₃OH on the methanol conversion, the production rate of CO and H₂O, and selectivity of CO₂. The methanol conversions for 240 and 300 °C are 42% and 73%, respectively, when the molar ratio of H₂O/CH₃OH is 0.4. The methanol conversion was increased with increasing molar ratio of H₂O/CH₃OH up to 1.2, and then decreased. This finding corresponds to that reported by Su and Rei¹³ because the methanol and water competed simultaneously with the active site of the catalyst. However, this trend would become masked when the temperature increased because the reaction rate of methanol reforming increased.¹⁴ The trend of hydrogen production rate was similar to that of methanol conversion. However, the CO₂ selectivity was increased with increasing molar ratio of H₂O/CH₃OH. It is demonstrated that the

Table 2. Methanol Reformation for Using Helium and Air^a

carrier gas	X_M	S_{CO_2}	V_{H_2} (vol%)	V_{CO} (vol%)
He	73.0	98.9	48.0	0.122
Air	93.5	99.7	57.0	0.040

^a Reaction conditions: catalyst (R10:5:5) = 0.2 g, carrier gas = 15 sccm, WHSV = 14.4 h⁻¹, H₂O/CH₃OH = 1.2, T = 240 °C.

Table 3. Methanol Conversion and Selectivity of CO₂ for Different Compositions of the Catalyst and Temperatures^a

catalyst	240 °C		300 °C	
	X_M (%)	S_{CO_2} (%)	X_M (%)	S_{CO_2} (%)
Cu/ZnO/Al ₂ O ₃				
R15:15:05	0.802	98.57	0.999	94.50
R15:10:10	0.766	99.40	0.992	94.10
R15:15:10	0.637	98.68	0.978	96.36
R15:15:15	0.549	99.70	0.888	95.13
R20:10:10	0.730	99.14	0.980	95.45
R20:15:10	0.630	99.70	0.963	97.42
R20:15:15	0.716	99.05	0.967	80.21
R25:10:10	0.753	99.25	0.991	87.39
R25:10:15	0.700	99.72	0.961	92.80
R25:15:15	0.721	99.76	0.979	99.52

^a R20:10:10 is equal to R10:5:5.

water–gas shift reaction was enhanced as the molar ratio of H₂O/CH₃OH increased. According to this experimental result, the molar ratio of H₂O/CH₃OH was set at 1.2 as kinetic optimal value. In addition, the volumetric percentages of CO for 240 and 300 °C are nearly less than 1% and more than 1%, respectively. It is demonstrated that the lower operating temperature would obtain the lower CO volumetric percentage.

3.4. Effect of Weight Hourly Space Velocity (WHSV) and Weight of the Catalyst. The optimum methanol conversion was dependent on the WHSV, as shown in Figure 5. The methanol conversion and volumetric percentage of CO decreased when the WHSV increased. The hydrogen production rates for 240 and 300 °C had maximum values of 35% and 50%, respectively, when the WHSVs were 28.7 and 43.0 h⁻¹. However, the WHSV was set as 14.4 h⁻¹ because the methanol conversions for 300 and 240 °C were less than 95% and 73%, respectively when the WHSV was larger than 14.4 h⁻¹. Thus, the volumetric percentage of CO was around 0.5%.

In general, increasing the amount of the catalyst will increase the conversion of reactant and the yield of product for the same reaction conditions. These reaction conditions were chosen as catalyst = R10:5:5, WHSV = 14.4 h⁻¹, He = 50 sccm, H₂O/CH₃OH = 1.2, as shown in Figure 6. The incremental amount of the catalyst increased the methanol conversion and the hydrogen production rate at 240 °C. However, the volumetric percentage of CO had a maximum value when the catalyst weight was around 0.35 g at 300 °C, and did not appear maximum value at 240 °C. The volumetric percentage of hydrogen production for 240 and 300 °C were larger than 40% as the weight of catalyst was more 0.3 g. It is demonstrated that this reaction combined methanol reformation and synthesis reactions, which are reversible reactions. When the temperature is high and the methanol retention time is high (i.e., the amount of the catalyst is greater), one can readily observe these reactions. Therefore, increasing the amount of the catalyst is really not necessary to obtain a good methanol reformation.

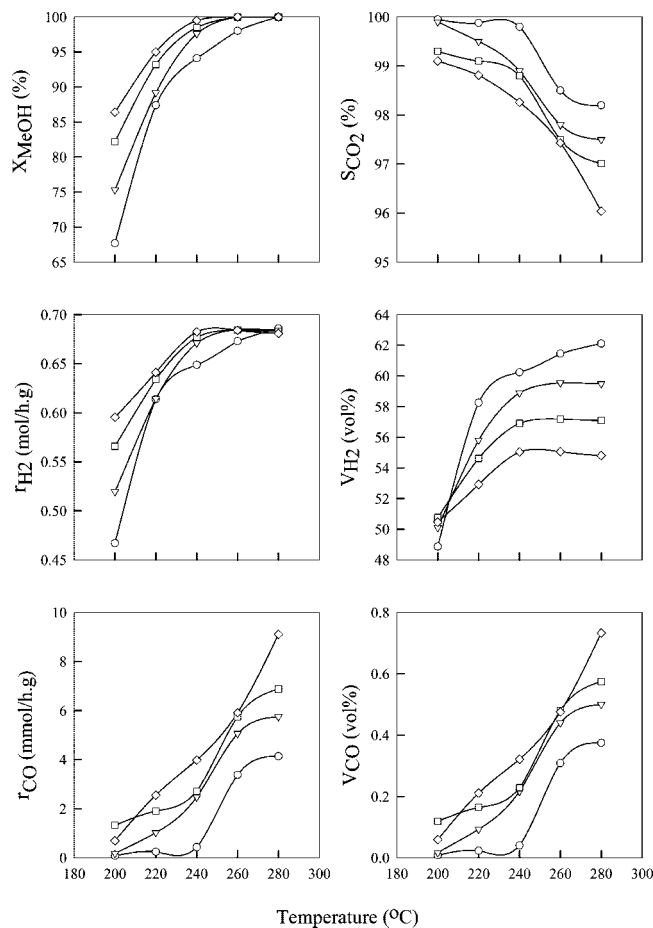


Figure 7. Effect of air content or temperature on methanol reformation. Catalyst (R10:5:5) = 0.3 g, WHSV = 14, 4 h⁻¹, H₂O/CH₃OH = 1.2; (O) 15 sccm, (V) 20 sccm, (□) 25 sccm, (◇) 30 sccm.

3.5. Effect of Carrier Gas. Two carrier gases, He and air, were used to test the methanol reformation. The flow rate of He was in the range of 15 to 80 sccm. In this range, the methanol conversion and the hydrogen production rate were not obviously changed for 240 and 300 °C, and the selectivity of CO₂ and volumetric percentage of CO for 240 °C remained 99% and 0.2%, respectively. However, the volumetric percentage of CO for 300 °C would be larger than 1% when the flow rate of He was smaller than 40 %. Therefore, the preferred flow rates of carrier gas He to be conducted in this case were 15 sccm at 240 °C and 50 sccm at 300 °C.

In general, the carrier gas was used with inert gas, such as helium and nitrogen, to avoid gas reaction with methanol. However, the cost of carrier gas will increase in industrial application. Hence, if the carrier gas could be replaced with air, the system cost could be reduced, but the methanol reformation would become partial oxidation or autothermal reaction. If the inlet flow rate of air was 15 sccm, and the flow rate of methanol was limited at 0.046 mol/h, the molar ratio for both would be 0.08. In this condition, the reaction is always a steam methanol reformation because most oxidation methanol reformation was operated with the flow rate ratio of air to methanol more than 20%. Table 2 lists the methanol conversion and the selectivity of CO₂ for carrier gas of helium and air at 240 °C. The methanol conversion,

Table 4. Methanol Conversion and Selectivity of CO₂ at Different Reaction Conditions as Reported in the Literature

catalyst	carrier gas	temperature (°C)	X _M (%)	S _{CO₂} (%)	reference
Cu/ZnO/Al ₂ O ₃	air	240	97.6	99.7	this study
	He	240	73.0	95.4	
	N ₂	250	40.0	99.0	Johan et al. ¹⁵
	Air	250	50.0	99.0	
	He	240	38.0	99.0	Yongaek and Harvey ¹⁴
	N ₂	260	58.4	99.0	Liu et al. ¹⁶

Table 5. Surface and Kinetic Properties of Different Cu/ZnO/Al₂O₃ Catalysts^a

Cu/ZnO/Al ₂ O ₃	Cu size (nm)	Cu surface area (m ² /g catalyst)	dispersion (%)	BET area (m ² /g)	X _M (%)	A _A (mmol/h)	TOF (s ⁻¹)
R15:15:5	14.6	17.9	8.25	71	80.2	185	0.092
R15:15:5 ^b	14.6	17.9	8.25	71	97.2	224	0.112
R15:10:10	15.3	16.0	7.41	49	76.6	176	0.098
R20:10:10	17.4	17.5	6.93	41	73.0	168	0.086
R25:10:10	22.2	15.2	5.42	52	75.3	173	0.110
R25:15:15	17.9	15.5	6.76	38	72.1	166	0.095

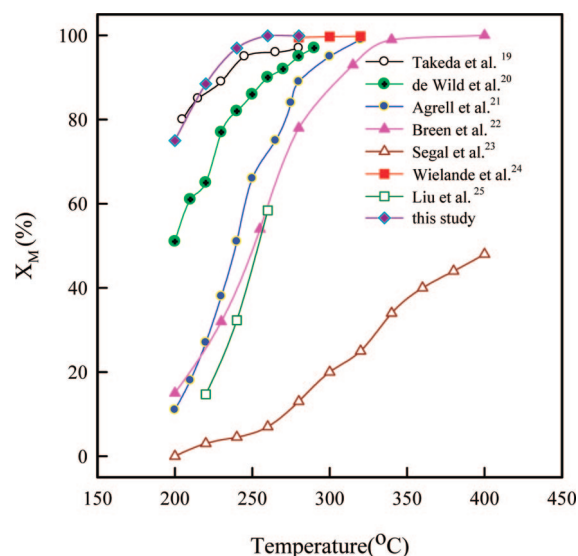
^a Reaction for catalyst = 0.2 g, He = 50 sccm, WHSV = 14.4, H₂O/CH₃OH = 1.2 at 240 °C. ^b Reaction for catalyst = 0.3 g, air = 20 sccm, WHSV = 14.4, H₂O/CH₃OH = 1.2 at 240 °C.

the volumetric percentage of hydrogen and CO were changed from 73% to 93.5%, 48% to 57%, and 0.122% to 0.04%, respectively. This finding demonstrates that using air to carry methanol is a good method and increases the reaction reactivity, which could result in a higher volumetric percentage of hydrogen (>50 %) and lower volumetric percentage of CO (<500 ppm).

3.6. Optimal Reactivity of Methanol Reformation. The catalyst R10:5:5 was first screened by combinational chemistry method as mentioned in Section 3.1. In this section, change the name of the catalyst R10:5:5 to R20:10:10. Furthermore, the composition of Cu/ZnO/γ-Al₂O₃ was changed and different from R20:10:10 with the ratio interval of 5, nine catalysts prepared were obtained, and conducted in the methanol reformation to screen the reactivity of the catalyst, as listed in Table 3. The experimental result shows the reactivity of the catalyst R15:15:5 was the best among nine catalysts, and even larger than that of the catalyst R10:5:5. The methanol conversion was increased from 0.73 to 0.802. Hence, the methanol reformation using catalyst R15:15:5 was carried out with air, as shown in Figure 7.

Figure 7 shows the effect of air flow rate (15–30 sccm) and reaction temperature (200–280 °C) on methanol reformation. The results for air of 20 sccm were obtained as follows: methanol conversion was 97.6 %, the production rate and volumetric percentage of hydrogen were 0.671 mol/h·g and 59%, and the production rate and volumetric percentage of CO were 2.25 mmol/h·g and 0.21 %, respectively. The results for the other flow rate also obtain the same trend as shown in Figure 7, even though the temperature is 200 °C. Most reactions were of high hydrogen production rate and high CO production rate as the temperature was high. However, all volumetric percentages of CO were small than 1% for all operating cases in Figure 7. This experimental result is the best one comparing with the literature as shown in Table 4.

Table 5 summarizes the size, dispersion, and BET surface area of copper catalyst and turnover frequencies for the steam reforming of methanol at various catalysts prepared in this work. The surface area was measured by nitrogen adsorption with BET method. The conversion of methanol increased

**Figure 8.** Plot of methanol conversion on temperature comparing with literature data, which were quoted with the report of Basile et al.¹⁸

with increasing BET surface area of the catalyst. The maximum conversion (97.2%) was obtained when the surface area of R15:15:5 catalyst was 71.1 m²/g. Meanwhile, the Cu size and dispersion of the catalyst R15:15:5 were the minimum (14.6 nm) and maximum (8.25%) values, respectively, in Table 5. The turnover frequency was about 0.085–0.11 with helium as carrier gases, and particularly higher values were obtained as the reforming system was introduced with air. These values (e.g., 0.11 s⁻¹) are larger than those (0.0152 s⁻¹) reported by Iwasa et al. using Cu/ZnO/Al₂O₃.¹⁷ On the other hand, Figure 8 shows a comparison of methanol conversion vs temperature of the catalyst R15:15:5 with literature data. The different behavior of each cited work is certainly due to the different operating conditions adopted by each author. However, the methanol conversion of this composition of the catalyst is the best one among these cases. Therefore, using the combinational chemistry method is easy to obtain an optimum composition in the methanol reformation.

4. Conclusions

The catalytic performance of methanol reformation using Cu/ZnO/ γ -Al₂O₃ as catalyst was studied in obtaining the best composition of the catalyst. The performance of the catalysts was screened by using high-throughput screening of combinatorial chemistry method. The catalyst R10:5:5 had the best activity among 27 catalysts. Furthermore, based on Cu/ZnO/Al₂O₃ ratio close to R10:5:5 to design 9 other catalysts, we found R15:15:5 with the highest catalyst activity. This catalyst can be used at operating temperatures below 240 °C. This experimental result for methanol conversion was better than those of the previous works.^{19–25}

Notation

A_{Cu} = activity of copper (mmol/g·h)
 C = catalyst made by coprecipitation
 Cu = copper
 F_{H_2} = molar flow rate of hydrogen (mmol/h)
 P = catalyst made by polyol method
 H_2 = hydrogen production rate per g catalyst (mol/h·g)
 R = catalyst made by oxalic coprecipitation
 R15:15:5 = weight composition of Cu, Zn, and Al made by oxalic coprecipitation was 15:15:5
 S_{CO_2} = selectivity of carbon dioxide
 T = absolute temperature (K)
 TOF = turnover frequency (s⁻¹)
 V_{CO} = carbon monoxide volumetric percentage (%)
 V_{H_2} = hydrogen volumetric percentage (%)
 WHSV = weight hourly space velocity (h⁻¹)
 X_M = methanol conversion (%)
 ZnO = zinc oxide
 Subscripts
 0 = initial
 CO = carbon monoxide
 CO₂ = carbon dioxide
 H₂ = hydrogen
 I = component *i*
 Total = total chemicals of CO, CO₂, H₂, and methanol
 M = methanol

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