Ethanol CO_2 Reforming over Cu/Al_2O_3 Catalyst for Syngas Production

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Abstract— ethanol CO2 reforming (ECR) over 10%Cu/Al2O3 catalyst was investigated for production of syngas. The catalyst was synthesized by implemented incipient wetness impregnation method and characterized by using X-ray diffraction (XRD). ECR was evaluated in a stainless steel fixed-bed reactor by varying reaction temperature from 973 K to 1023 K. XRD analysis indicated the formation of CuO phases and eventually reduce to Cu metallic during H2 reduction. The ethanol and carbon dioxide conversion reached until 55.39% and 38.91% respectively at 1023 K reaction temperature. Furthermore, H2/CO ratio was obtained below 2 which is ideal for Fisher-Tropsch synthesis (FTS).

Keywords—Ethanol; CO_2 reforming; Catalysts; Temperature; Syngas

1. INTRODUCTION

The dependence on fossil fuels to achieve energy requirements create negative impacts towards environments such as global warming and the released of greenhouse gases. Fossil fuels also categorize as nonrenewable sources which can diminished in the future. Therefore, there is a dire need of renewable and environmentally friendly energy sources to fulfill the upcoming energy demands.

Therefore, introduction of ethanol as feedstock is an optimistic option due to its affordable cost, high availability and low toxicity [1-3]. In addition, ethanol can be converted into valuable syngas by applying ECR technology. ECR is eco-friendly and an innovative way for syngas production because of consuming bio-ethanol and capable in utilizing the unwanted greenhouse gas which is CO_2. Synthetic gas produced from ECR can be applied for the downstream production of higher chain hydrocarbons through Fischer-Tropsch reaction and methanol production [4,5].

$$C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2 (\Delta H^\circ_{rxn} = 296.7 \text{ kJ mol}^{-1}) \quad (1)$$

Syngas can be produced from different approaches such as steam reforming, partial oxidation and autothermal reforming [6]. Nevertheless, these technologies comprise the involvement of non-renewable source which is methane (CH_4) and huge amount of CO_2 emissions. Therefore, with the introduction of ECR that operated ethanol and CO_2 as feedstock appears to be a notable option to replace natural resources.

Ni-based catalyst gain attention for reforming of ethanol because of its ability to break C-C bond. However, Ni-based catalysts usually deactivated due to the deposited carbon and sintering [7,8]. Hence, it is crucial to explore another type of metals such as copper to be implemented in this study. Additionally, catalytic performances hugely depend in operating conditions especially operating temperature. Thus, it is important to study the effect of operating temperature towards reactant conversions and product yields.

Currently, there is no previous research about Cu/Al_2O_3 catalyst on ECR reaction. Hence, it is very essential to study the catalytic performance of Cu/Al_2O_3 for ECR process. Therefore, the objective of this research is to study the influence of operating temperature of ECR process on $10\%Cu/Al_2O_3$.

2. EXPERIMENTAL

The γ-Al_2O_3 support (Puralox TH 100/150 from Sasol) was calcined to maintain the thermal stability of the support in carbolite furnace at 1023 K for 6 h using 5 K min^{-1} heating rate. The $10\%Cu/Al_2O_3$ catalyst was synthesized by using incipient wetness impregnation. The alumina support was impregnated with calculated amount of $Cu(NO_3)_2.3H_2O$ aqueous solution (supplied by Sigma-Aldrich) to obtain $10\%Cu/Al_2O_3$ catalyst. Thereafter, the mixture was stirred using rotary evaporator (BÜCHI Rotavapor R-200) under vacuum for 3 h at 323 K and later dried in oven overnight (UFB-500) at temperature of 393 K. Then, the dried catalyst was further calcined in air for 5 h at 873 K with 5 K min^{-1} ramping rate. The calcined catalyst was crushed and sieved for ECR evaluation.

For this study, XRD analysis was performed employing Cu monochromatic X-ray radiation accompanied by 1.5418 Å wavelengths (λ) at 30 kV and 15mA on a Rigaku Miniflex II system. The step increment of 0.02° was applied and the XRD patterns were noted from 3° until 80°. Match! Software was applied to analyze the data obtained.

ECR was performed in a fixed-bed reactor and situated in a tubular furnace at 20 kPa with reaction temperature of 948-1023 K. About 0.1 g of catalyst was placed inside the reactor using quartz wool. Ethanol was injected into the reactor from KellyMed KL-602 syringe pump whilst CO_2 reactant and N_2 gas were precisely controlled by mass flow controller (Alicat) catalyst was reduced first for 2 h at reduced at 973 K with 50 ml min^{-1} of $50\%H_2/N_2$ reducing mixture before reaction. Thereafter, ethanol and CO_2 at stoichiometric $C_2H_5OH:CO_2$ feed ratio of 1:1 was passed through the reactor at 42 L g_{cat}^{-1} h^{-1} of gas hourly space velocity (GHSV). Throughout 8 h of reaction, the total flow rate was retained at 70 ml min^{-1}. Then, the effluent gas was evaluated on gas chromatograph (GC) (Agilent GC 6890)

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD analyses for γ-Al_2O_3 and $10\%Cu/Al_2O_3$. The calcined γ-Al_2O_3 provided to make comparisons with other catalyst. The peak for γ-Al_2O_3 at 2θ recorded of 32.67°, 37.34°, 45.65°, and 67.02° (JCPDS card No. 04-0858) [9]. Meanwhile, for $10\%Cu/Al_2O_3$, CuO phase was detected at 2θ of 32.53°, 35.56°, 38.75°, 48.75°, 58.36°, 61.57°, 75.28° (JCPDS card No. 41-0254) [10].

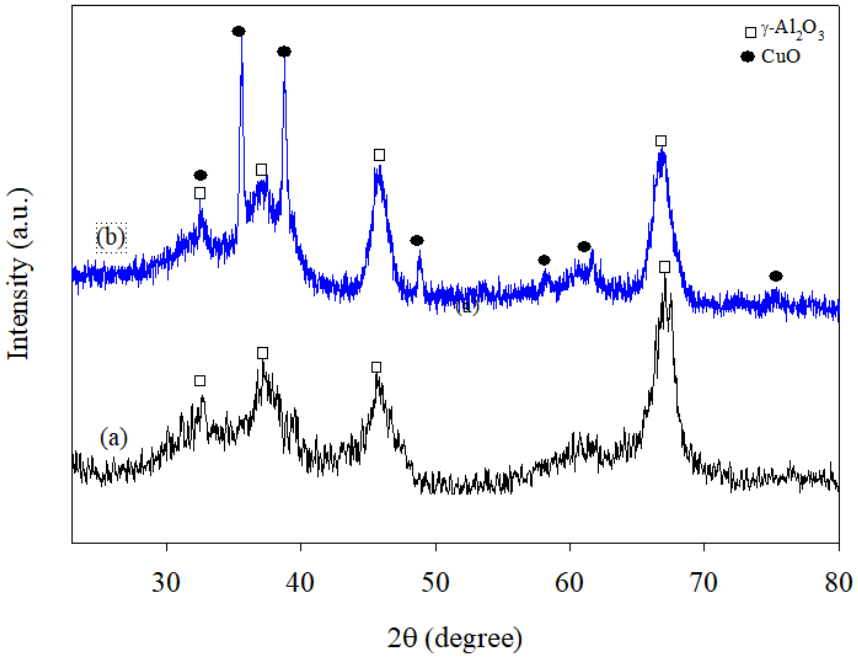

Figure 1: XRD analysis of fresh (a) γ-Al_2O_3 (b) 10%Cu/Al_2O_3

The outcome on temperature effect of ECR on catalytic performance was investigated at stoichiometric feed ratio which is $P_{CO_2} = P_{C_2H_5OH}$ = 20 kPa by varying reaction temperature from 973 K until 1023 K. Fig. 2 shows the effect of temperature on ethanol and carbon dioxide conversion over 10%Cu/Al_2O_3 catalyst. Based on results, the trend visibly indicated upwards trend as the temperature increase. The highest conversion of ethanol and CO_2 obtained at temperature 1023 K followed by 998 K and 973 K. Furthermore, at temperature 1023 K the ethanol and CO_2 conversions are 53.2% and 37.2% % respectively. This is due to the endothermic nature of ECR process that favors high temperature reaction [11].

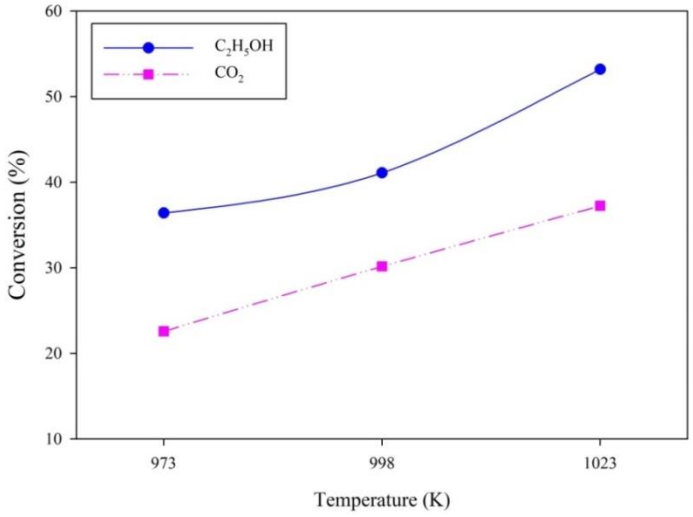

Figure 2: Temperature effect on ethanol and CO_2 conversion over 10%Cu/Al_2O_3 catalyst at $P_{CO_2} = P_{C_2H_5OH}$ = 20 kPa.

The effect of temperature on product yield over 10%Cu/Al_2O_3 catalyst was presented in Fig. 3. The product yield for H_2, CO and CH_4 shows trend aligned with the increasing temperature. Moreover, highest yield for hydrogen at 1023 K with 31.7 %, 20.3% of CO yield and 10.8% for CH_4. These trend previously reported by Jankhah and Abatzoglou (2008) that credit enhance of the CH_4 dry reforming reaction. CH_4 yield proposed similar increasing trend due to rate of ethanol decomposition is relatively higher compared to methane dry reforming with increasing temperature [12].

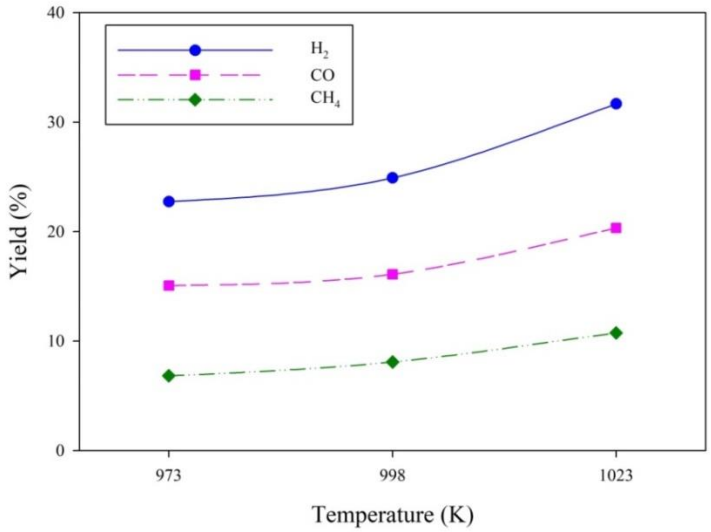

Figure 3: Temperature effect on product yield over 10%Cu/Al_2O_3 catalyst at $P_{CO_2} = P_{C_2H_5OH}$ = 20 kPa.

Fig. 4 indicates the H_2/CO and CH_4/CO ratio from temperature effect of ECR reaction for 10%Cu/Al_2O_3 catalyst. H_2/CO ratio improves with enhancement of temperature and the ratio greater than 1 because of concurrent ethanol dehydrogenation reaction during ECR process [13]. H_2/CO ratio varied from 1.51 until 1.56 which is acceptable for Fisher-Trospch synthesis [14]. The enhancement CH_4/CO ratio with the increasing of temperature is because of ethanol decomposition is more active compared to reforming of methane.

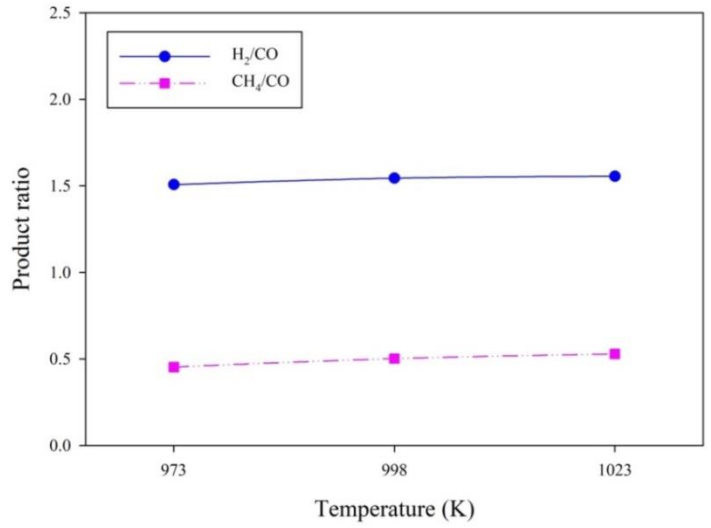

Figure 4: Temperature effect on product ratio over 10%Cu/Al_2O_3 catalyst at $P_{C2H5OH} = P_{CO2}$ = 20 kPa.

4. CONCLUSIONS

10%Cu/Al_2O_3 catalyst has been evaluated for ECR reaction at different reaction temperature of 973 K to 1023 K with constant ethanol and carbon dioxide partial pressure. ECR undergo 8 h reaction time. From XRD results, CuO phase was dispersed throughout the surface of catalyst with crystallite size of 32.4 nm. The performance of 10%Cu/Al_2O_3 based on reaction temperatures are as follow 1023 K > 998 K > 973 K. The ethanol and carbon dioxide conversion reached until 53.2% and 37.2% respectively at temperature of 1023 K. In addition, product yield and H_2/CO ratio also rise with increasing of temperature. H_2/CO ratio > 1 represents the availability of ethanol dehydrogenation.

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