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**Ethanol CO<sub>2</sub> Reforming on Al<sub>2</sub>O<sub>3</sub>-supported Cu-based Catalyst for Syngas Production**

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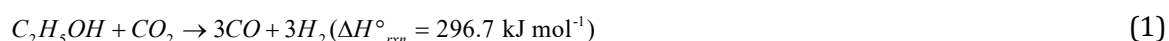
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**EXTENDED ABSTRACT**

The dependence on fossil fuels to meet energy demands has led to future insecurity of non-renewable energy sources [1]. Hence, there is a dire need of renewable and environmental friendly energy sources to fulfill the future energy demands. Ethanol is emerged as a potential alternative due to its affordable cost, renewability, high availability and low toxicity [2, 3, 4]. In addition, ethanol can be converted to valuable synthetic gas (syngas) using ethanol CO<sub>2</sub> reforming (ECR) technology. ECR is an eco-friendly and a novel way for syngas production because it not only consumes bio-ethanol but also offers an additional benefit by utilizing the unwanted greenhouse gas (CO<sub>2</sub>). Synthetic gas produced from ECR can be employed for the downstream production of higher chain hydrocarbons through Fischer-Tropsch reaction and methanol production [5,6]. This study investigates the effect 10%Cu/Al<sub>2</sub>O<sub>3</sub> catalyst for ECR at 973 K for 6 h time-on-stream. ECR produces a mixture of hydrogen (H<sub>2</sub>) and carbon monoxide (CO) labeled as an equimolar syngas from reaction between ethanol and carbon dioxide based on Eq. (1)



The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Puralox TH 100/150 from Sasol) was calcined to maintain the thermal stability of the support in a muffle carbolite furnace at 1023 K for 6 h employing a heating rate of 5 K min<sup>-1</sup>. The 10%Cu/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by using incipient wetness impregnation. The alumina support was impregnated with calculated amount of aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (supplied by Sigma-Aldrich) to obtain 10%Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. Thereafter, the mixture was stirred using rotary evaporator (BÜCHI Rotavapor R-200) at 323 K for 3 h under vacuum and later dried overnight in oven (UFB-500) at 393 K. Then, the dried catalyst was further calcined in air at 873 K for 5 h with ramping rate of 5 K min<sup>-1</sup>. Finally, the calcined catalyst was crushed and sieved to 140-250  $\mu$ m particle range for ECR evaluation.

ECR was carried out in a stainless steel fixed-bed reactor and placed vertically in a tubular furnace at 20 kPa with reaction temperature of 973 K. About 0.1 g of catalyst was placed at the centre of the reactor using quartz wool. Ethanol was injected into top of the reactor by syringe pump (KellyMed KL-602) whilst CO<sub>2</sub> reactant and N<sub>2</sub> diluent gas were precisely regulated by Alicat mass flow controller. Prior to the reaction, the catalyst was reduced at 973 K with 50 ml min<sup>-1</sup> of 50%H<sub>2</sub>/N<sub>2</sub> reducing mixture for 2 h. Thereafter, ethanol and CO<sub>2</sub> at stoichiometric C<sub>2</sub>H<sub>5</sub>OH:CO<sub>2</sub> feed ratio of 1:1 was passed through the reactor at gas hourly space velocity (GHSV) of 42 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. The total flow

rate was kept constant at 70 ml min<sup>-1</sup> for 6 h of reaction. Then, the effluent gas was analyzed on Agilent GC 6890 series gas chromatograph (GC) equipped with thermal conductivity detector (TCD).

Figure 1 shows the catalytic performance of ECR process on 10%Cu/Al<sub>2</sub>O<sub>3</sub> with 6 h time-on-stream. The conversion of ethanol and CO<sub>2</sub> was recorded around 80.37% and 37.42%, respectively. The catalyst appears to be stable throughout the reaction. The conversions of ethanol are significantly higher compared to CO<sub>2</sub> conversions because of the occurrence of ethanol decomposition (Eq. (2)) and ethanol dehydrogenation (Eq. (3)) [8, 9]. The yield of H<sub>2</sub> was recorded about 63.05% whereas the yield for CO was about 32.28% as shown in Fig. 1(b). In addition, H<sub>2</sub>/CO ratio calculated was approximately close to 2, which is highly suitable for the Fisher-Tropsch reaction.

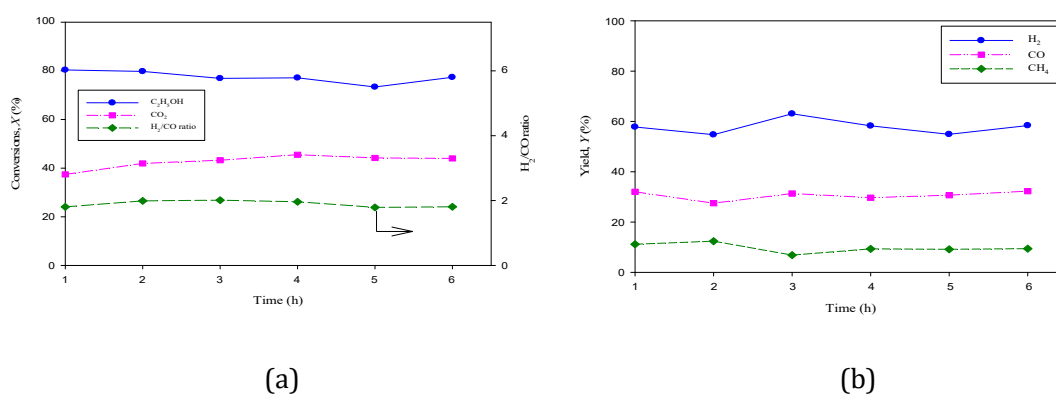
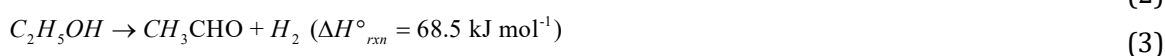
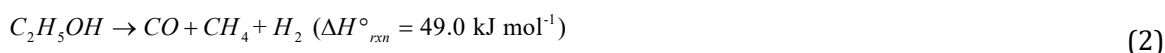


Figure 1. (a) Reactant conversions and H<sub>2</sub>/CO ratio and (b) product yields with time-on-stream during ECR on 10%Cu/Al<sub>2</sub>O<sub>3</sub> catalyst at T = 973 K and stoichiometric feed composition,  $F_{CO_2} =$

$$F_{C_2H_5OH} = 1:1$$

Keywords: Ethanol; CO<sub>2</sub> reforming; Cu-based catalysts; Hydrogen; Syngas

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