

Methanol Synthesis in a Slurry Phase Reactor over Cu/ZnO/Al₂O₃ Catalyst

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Abstract. Methanol synthesis from synthesis gas (syngas, a mixture of hydrogen (H₂) and carbon monoxide (CO)) in the presence of copper/zinc oxide/alumina catalyst (Cu/ZnO/Al₂O₃) was investigated using semi-batch reactor. The process was operated at 280 °C under pressure 40 bar in a slurry reactor (Parr reactor model 4848). The catalyst weight, syngas molar ratio and residence time were optimized for methanol synthesis. Cu/ZnO/Al₂O₃ catalyst was prepared by a two-step surfactant assisted precipitation method using polyethylene glycol (PEG 6000). The catalyst's surface area, crystallinity, reducibility and morphology were characterized by BET, XRD, H₂-TPR and SEM-EDS, respectively. The BET analysis indicated that the catalyst calcined at 300 °C gave the highest surface area (99.67 m²/g). The crystallite size of Cu in Cu/ZnO/Al₂O₃ catalyst was estimated to be 14.14 nm., after adding the surfactants. The maximum methanol yield (607.53 g_{CH₃OH}/Kg_{cat}·h) was achieved after 24 hours of residence time using 5 g of the catalyst under a stream of 2 to 1 molar ratio of H₂ and CO reactive mixed gas. Under these conditions, 38.26% of CO conversion and 93.11% of selectivity to methanol were achieved. When the residence time was decreased to 12 hours with molar ratio of 0.5 H₂ to 1 CO, the yield of methanol was 388.11 g_{CH₃OH}/Kg_{cat}·h, with a CO conversion of 38.53% and selectivity to methanol of 90.77%.

1. Introduction

Alternative fuels and renewable energies receive continued attention due to the issues of global warming and energy security. Methanol is both a potential alternative fuel and a basic building block for producing derivatives such as biodiesel, methyl tertiary butyl ether (MTBE), formaldehyde, dimethyl ether (DME) and acetic acid. It can be used as a transportation fuel such as M85 (a mixture of 85% methanol, 15% unleaded gasoline). Thus, methanol is an important chemical and attractive as a fuel since it burns cleanly forming no particulate matter and causes less carbon than traditional fuels [1]. Commercially, methanol is produced by reacting synthesis gas over a Cu/ZnO/Al₂O₃ catalyst at 50-100 bar and 200-300 °C [2, 3]. The fundamental steps of methanol synthesis consisting CO hydrogenation (Eq.1), CO₂ hydrogenation (Eq.2) and water-gas shift reaction (Eq.3) can be written as follow: [4].



These reactions take place on heterogeneous surface and relate with carbon deposition. CO₂ in the feed gas helps to prevent the catalyst from deactivation. Without the CO₂ in feed gas, the carbon deposition can be occurred via Boudouard reaction (Eq.4) [5, 6].



A ternary Cu/ZnO/Al₂O₃ catalyst has been widely used in methanol synthesis, [7] catalyst is synthesized using various methods such as co-precipitation, impregnation, sol-gel and two-step precipitation method using surfactant assisted. In this work, two-step precipitation was chosen as a preparation method since it generally provides a higher catalytic surface area. The surfactant is reported to reduce the surface tension of Cu resulting in a smaller crystallite size of the catalyst, leading to its higher surface area [8, 9].

The gas phase methanol synthesis, which is normally carried out in a packed-bed reactor because of simplicity [10]. Nevertheless, it has some disadvantages, one of which is low conversion (15-25%) due to the hotspots occurring in the packed-bed of the catalyst caused by poor heat transfer. The slurry phase reactor avoids this problem and has a number of advantages such as simple temperature control, high heat transfer rate, high conversion (50-70%) [8,11], low pressure operation and low catalyst usage, however, the main problem of the slurry phase methanol synthesis is the catalyst's deactivation [11,12].

In this work, Cu/ZnO/Al₂O₃ catalyst was prepared by the two-step surfactant (polyethylene glycol, PEG 6000) assisted precipitation method. The catalyst was characterized by N₂-sorption, XRD, SEM-EDS and H₂-TPR methods. The catalyst weight (5-40 g), syngas molar ratio (0.5 and 2) and residence time (6-30 hours) were investigated to optimize methanol production.

2. Experimental

2.1 Preparation of Cu/ZnO/Al₂O₃ catalyst. The mass ratio of CuO: ZnO: Al₂O₃ were calculated to be 65: 25: 10. A mixture of copper nitrate and zinc nitrate were added drop-wise into sodium hydrogen carbonate solution with the 2% of surfactant at 75 °C until the pH approached 7.0. The binary mixture was aged for 1 hour and washed with deionized water at 75 °C to remove the residual sodium. The Al₂O₃ slurry support was prepared by adding 10% ammonia to aluminum nitrate solution. This mixture was then poured into the binary mixture of copper and zinc solution with vigorous stirring at 75 °C. The resulting ternary catalyst was washed with deionized water at 75 °C, filtered and dried overnight at 120 °C [8]. The effect of calcination temperature on the catalyst's surface area was investigated by preparing four batches of catalyst, calcined at either 100, 200, 300 and 350 °C for 2 hours. The catalyst was crushed and pressed into 20-40 mesh before being introduced into the reactor. After calcination, the catalyst was activated in a stainless steel fixed-bed reactor under 5% H₂/N₂ for 10 hours at 275 °C, followed by passivation flowing 1% O₂/N₂ for 10 hours at room temperature.

2.2 Characterization of Cu/ZnO/Al₂O₃ catalyst. The specific surface area was evaluated by N₂ sorption at -196 °C using the BET method (Quantachrome instrument model autosorb1). X-ray diffraction (XRD) was performed (shimadzu instrument model XD 6000), using CuK α radiation in the range of 10° < 2 θ < 80° operated at 40 kV, 40 mA. A scanning electron microscope combined with Electron Dispersive Spectrometer (SEM-EDS) analysis was conducted (JEOL model JEM 6340J) to examine topology of the catalyst's surface and to identify metal content in the catalyst. H₂-temperature programmed reduction (H₂-TPR) was performed using a BEL Japan, Inc, model Belcat-B to find the reduction temperature of Cu/ZnO/Al₂O₃; 65 mg of the calcined catalyst was reduced in a stream of 5% H₂/Ar at a flow rate of 40 ml/min, from room temperature to 500 °C at a heating rate 10 °C/min. The hydrogen consumption was monitored online by a thermal conductivity detector (TCD).

2.3 Methanol synthesis reaction. Methanol synthesis by the reaction of synthesis gas over Cu/ZnO/Al₂O₃ catalyst was performed in a 0.25 m³ of slurry phase semi-batch reactor (Parr reactor model 4848). The catalyst's weight was varied from 5 to 40 g. The chosen quantity of catalyst was added into 170 ml of paraffin oil which acted as an initial liquid media. 50 ml/min of reactive gas (63% H₂, 32% CO, 5% CO₂, by volume) was introduced into the reactor, operated at 280 °C, 40 bar and stirred at 1000 rpm for 30 hours. Synthesis gas with the composition of H₂:CO:CO₂:N₂ = 30:60:5:5 was also used as a feedstock to mimic the composition of syngas produced by a biomass

gasification plant operated at the Thailand Institute of Scientific and Technological Research (TISTR). The products were sampled for analysis every 6 hours. The effluent gas was passed through a hot trap, followed by a cold trap and back pressure regulator before analyzed by gas chromatography. The condensed liquid products were analyzed by GC-FID using a DB-WAX column. The gaseous products (H_2 , CO , CO_2 and CH_4) were investigated by GC-TCD using a WG-100 and Unibeads column.

3. Results and discussion

3.1 Cu/ZnO/ Al_2O_3 catalyst characterization. Fig.1 shows the effect of calcinating temperatures (100 to 350 °C) on the catalyst surface area. The highest surface area of the catalyst, 99.67 m^2/g , obtained at a calcinating temperature of 300 °C. At calcinations temperature lower than 300 °C, the surface area was found to increase due to the evaporation of volatile, water and salts residuals on the catalyst surface. At temperature higher than 300 °C, the surface area decreased owing to sintering of the catalyst. Following this result, all of lab-prepared Cu/ZnO/ Al_2O_3 catalyst samples were calcinated at 300 °C for 2 hours.

The XRD pattern of reduced catalyst is shown in Fig.2. The diffraction peaks of Cu appeared at $2\theta = 43.4^\circ$, 50.5° and 74.2° and diffraction peaks of ZnO located at $2\theta = 31.9^\circ$, 62.8° and 67.9° respectively [8]. The crystallite size, calculated by Scherrer's equation, of Cu in the reduced catalyst is 14.14 nm. approximately.

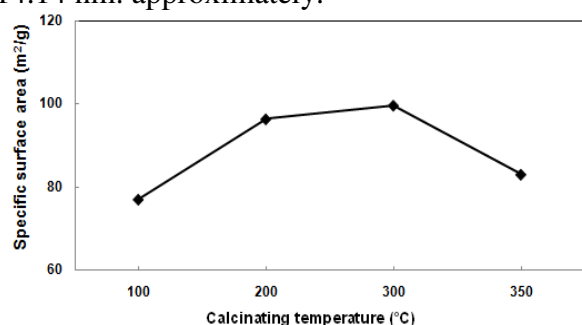


Fig.1 The effect of calcinating temperature catalyst to catalyst's surface area

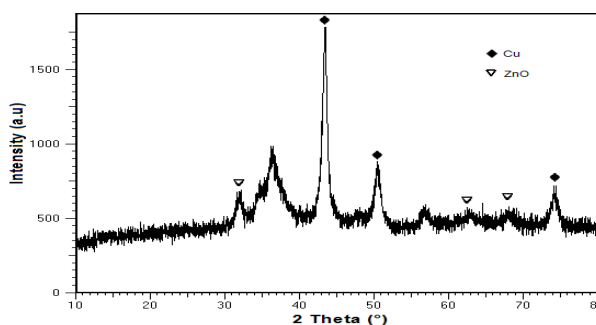


Fig. 2 XRD pattern of Cu/ZnO/ Al_2O_3

Fig.3 shows the morphology of calcined catalyst analyzed by SEM. The image illustrated that the catalyst's particles are spherical and considered small (1-2 μm .) which resulted in its large surface area. The mass ratio of calcined Cu/ZnO/ Al_2O_3 catalyst was confirmed as 57.30% of Cu, 19.78% of Zn, 7.76% of Al and 15.16% of O_2 , using the EDS technique.

The reducibility analysis of the catalyst was carried out at 275 °C by TPR method. Fig. 4 shows a single reduction peak of the prepared catalyst, corresponding to the Cu^{2+} to Cu^0 . The reduction temperature was found to be in the range of 220-260 °C. This is possibly due to a strong interaction between CuO and ZnO in Cu/ZnO/ Al_2O_3 , caused by the effect of the surfactant addition. This led to higher reduction temperature, compared to others research works [8, 13, 14].

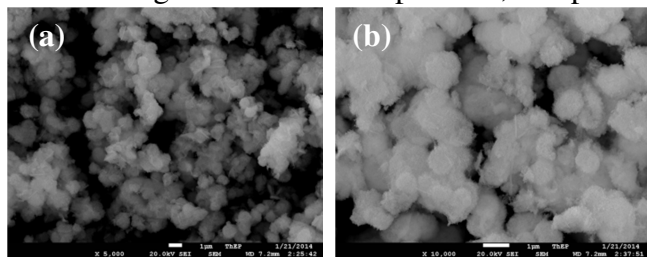


Fig.3 SEM image of Cu/ZnO/ Al_2O_3 catalyst
(a) 5000x magnification and (b) 10000x magnification

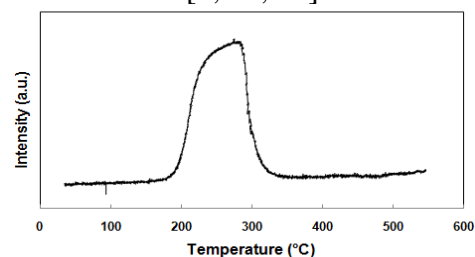


Fig.4 TPR profile of Cu/ZnO/ Al_2O_3 catalyst

3.2 Methanol synthesis. Fig.5 shows methanol yield obtained by 4 batches of the reaction conducted using catalyst's weight of 5, 10, 25 and 40 g. The results indicated that 5 g of catalyst (♦) gave the greatest yield of methanol between 6 to 30 hours of residence time. The highest methanol yield, 607.53 $g_{CH_3OH}/Kg_{cat} \cdot h$, 38.26% CO conversion and 93.11% selectivity were obtained at a

residence time of 24 hours using 5 g of catalyst. When the syngas molar ratio was altered to $H_2: CO = 0.5$, the maximum methanol yield, obtained in this case, was $388.11 \text{ g}_{CH_3OH}/Kg_{cat} \cdot h$ over 5 g of catalyst occurred after 12 hours residence time with 38.53% CO conversion and 90.77% selectivity, represented by the dotted line. The CO conversion was considered low compared to other works [8, 11]. This is possibly due to the heat and mass transfer limitations in the reactor caused by unsuitable mixing technique.

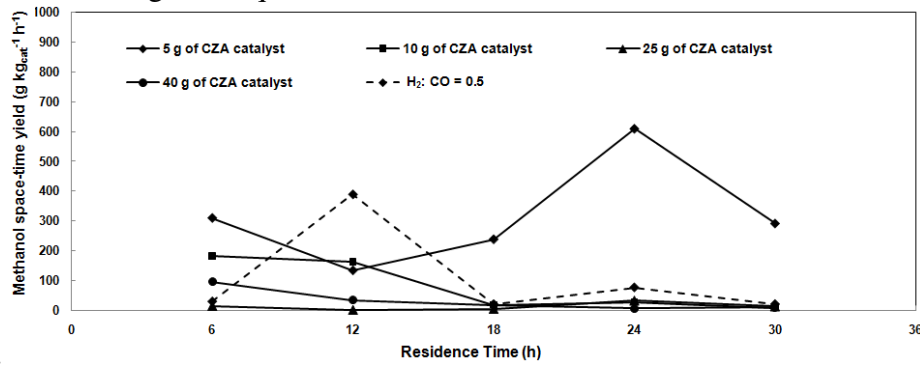


Fig. 5 The effect of residence time (6, 12, 18, 24 and 30 h) on methanol space time yield over 5, 10, 25 and 40 g of Cu/ZnO/Al₂O₃ catalyst in a slurry phase reactor.

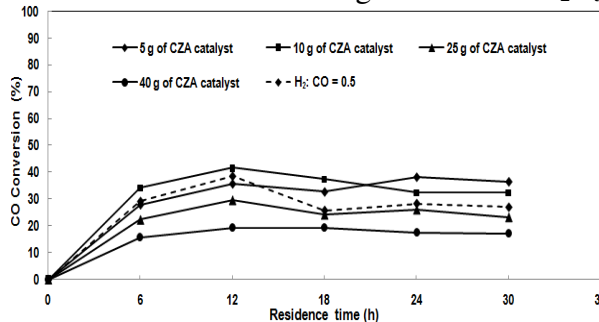


Fig. 6 The effect of residence time on CO conversion

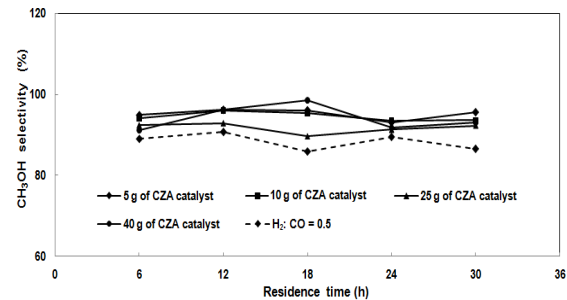


Fig. 7 The effect of residence time on methanol selectivity

Fig. 6 shows a relation between CO conversion and residence time. CO conversion was found to be stable, for all weight of the catalyst, after 18 h of reaction. The reaction over 5 and 10 g of catalyst gave greater CO conversion compared to the reaction over 25 and 40 g of the catalyst. The noticeably unstable CO conversion in the early period of reaction, from 6 to 18 h, was possibly caused by the associated water gas shift reaction (Eq. 3) and also thermodynamic limitation due to accumulated heat of the reaction (that was released from the exothermic methanol synthesis reaction) in the reactor. The CO conversion was calculated from the below equation.

$$\text{CO conversion (\%)} = \left(\frac{N_{CO,i} - N_{CO,o}}{N_{CO,i}} \right) \times 100 \quad (5)$$

Where $N_{CO,i}$ = number of mole of CO at inlet
 $N_{CO,o}$ = number of mole of CO at outlet

The influence of residence time on methanol selectivity, over different weights of the catalyst's use, was shown in Fig. 7. The syngas molar ratio of 0.5 was found to give lower selectivity of methanol, to compare with the 2 to 1 molar ratio of H_2 and CO according to its stoichiometric suitability.

4. Conclusion

Crystallite size of Cu in the lab-prepared Cu/ZnO/Al₂O₃ catalyst was estimated to be 14.14 nm. Specific surface area ($99.67 \text{ m}^2/\text{g}$) of the catalyst was found to be relatively high. This was due to the preparation technique using PEG surfactant assisted precipitation method which helps reducing crystallite size and surface tension of Cu. This leads to an increase of the catalyst's surface area. The lab-prepared Cu/ZnO/Al₂O₃ catalyst displayed a good performance (approximately 38% CO

conversion and 90-93% methanol selectivity) towards the methanol synthesis in a slurry phase reactor.

The optimum weight of catalyst for methanol synthesis in this research is 5 g. Maximum methanol yield ($607.53 \text{ g}_{\text{CH}_3\text{OH}}/\text{Kg}_{\text{cat}} \cdot \text{h}$), 38.26% of CO conversion and maximum methanol selectivity (93.11%) were achieved after 24 hours of the residence time, when 2 to 1 molar ratio of H_2 to CO was used as a feedstock. Under a stream of syngas with 0.5 molar ratio of H_2 to CO, $388.11 \text{ g}_{\text{CH}_3\text{OH}}/\text{Kg}_{\text{cat}} \cdot \text{h}$ of methanol yield was obtained after 12 hours of residence time, with a CO conversion of 38.53% and selectivity to methanol of 90.77%.

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