**Effects of catalyst preparation on hydrogen production using copper-zinc oxide-alumina**

*Sopita Wichaidit*, Pawinee Eamprapai, Massupa Puangmalee, Choowong Chaisuk

Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, 73000, Thailand
*e-mail address: pang947@hotmail.com*

**Abstract** – This research, the effects of catalyst preparation method on hydrogen production using copper-zinc oxide-alumina was focused. The procedure for catalyst preparation of two techniques; flame spray pyrolysis (FSP) and solvothermal synthesis at the fixed metal/alumina ratio(1:1:8) The catalyst properties were mainly characterized using XRD, SEM, TEM and TPR. Incorporation by FSP shows higher H₂ production rate than others preparation method at the same metal/alumina ratio. The solvothermal catalysts seem to promote the partial oxidation of methanol at the operating condition in this work. Moreover, the impregnated catalyst improves CO (CO₂) hydrogenation and decomposition of methanol to cracking products and oxygenated compounds.

**Keyword:** H₂ production/ methanol/ Cu-ZnO-Al₂O₃/ flame spray pyrolysis/ solvothermal
1. Introduction

Currently, much attention is focused on fuel cells as a clean and efficient source of electrical power for both mobile and stationary applications [1]. Fuel cells need hydrogen or hydrogen-rich feed gas as fuel. Several proven technologies such as steam reforming, autothermal reforming, partial oxidation, decomposition and water gas shift can be used to extract hydrogen from fuels like gasoline, diesel, LPG, methane, ethanol and methanol [2]. Methanol can be produced from a variety of sources, including natural gas, coal, and biomass through a syngas-to-methanol route. However, the processes are not economical, but increased interest has recently been shown in these alternative routes.[3]

In fact, the vast majority of the investigations of hydrogen production from methanol have focused on steam reforming that has over the other methanol conversion methods in regard to low CO production does not translate to other hydrocarbon fuels. The steam reforming of methanol (SRM) can be classified as low and high temperature steam reforming. For Cu-based [4-6] and Pd-based [7-11] catalysts show good activity and selectivity to low temperature steam reforming. In this research, study effects of catalyst preparation method on hydrogen production using copper-zinc oxide-alumina.

2. Experiment

The details of the experimental system and procedures used in this research are classified into three sections.

2.1 Catalyst preparation

- Preparation by flame spray pyrolysis

Copper (II) nitrate, zinc chloride and aluminium nitrate were used as the feed precursor, which was diluted in ethanol 0.5 M solution. The mixed of precursor and solvent was injected through the center capillary of the FSP nozzle by a syringe pump at 5 ml/min. Oxygen was fed for dispersion of solution at 5 ml/min. The catalyst powder was collected on a glass microfiber filter with the aid of a vacuum pump.

- Preparation by sovolthermal synthesis

A 20 g of aluminum isopropoxide was mixed with 100 ml organic solvent (1,4 butandiol, parrafin or toluene) in the test tube. The gap between the test tube and the autoclave wall was filled with 30 ml of the same solvent. The autoclave was purged by nitrogen and heated up to 300 °C at a rate of 2.5 °C/min and held at 2 h. After the mixture was cooled down, the resulting product was repeatedly washed with methanol and centrifuged for several times. The alumina powder was dried at room temperature for 12 h and subsequently calcined in airflow at 600 °C for 6 h.

2.2 Catalyst characterization

The catalytic properties were characterized by various methods. The phase identification and the average crystalline size were determined by the X-ray diffraction technique (XRD). The morphology and image of the three-dimensional sample were focused by scanning electron microscope (SEM). The particle characteristics were focused by transmission electron microscope (TEM). The temperature programmed reduction (TPR) exhibited reduction behavior and reducibility of the catalysts. Samples were collected at 30 min in each temperature. The composition of the effluent was measured by online gas chromatograph equipment, GC-TCD and GC-FID.

2.3 Catalytic activity of hydrogen production from methanol

Catalytic activities of all samples were studied at a steady state in a fixed-bed reactor. For each experiment, 0.2 ml of the catalyst was packed in a fixed-bed reactor. The feed stream was produced through the saturator containing the liquid methanol and water. Prior to the catalytic activity test, the catalyst was reduced by hydrogen at 300 °C and held at this temperature for 1 h. The experiments were performed at atmospheric pressure, and range of temperature was 200-500 °C. The product samples were collected at 30 min in each temperature. The composition of the effluent was measured by online gas chromatograph equipment, GC-TCD and GC-FID.

3. Results and Discussion

Figure 1 shows the XRD patterns of Cu-ZnO-Al2O3 catalysts at Cu:ZnO:Al2O3 as 1:1:8 gave tenorite, zincite and gamma phase. For the tenorite phase was assigned by the dominant peaks at 36, 39, 49 and 62. The XRD peaks at 32, 34 and 36° were evident for the zincite phase and the XRD peaks at 32°, 37°, 39°, 45°, 61° and 66° were evident for the gamma phase.


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Figure 2 shows the shape of Cu-ZnO-Al2O3 catalyst with various preparation methods, as focused by SEM. The shape of Al2O3 was rather spherical and the particles consist of small thin plates.

Figure 3 shows the shape of particles for Cu and Al2O3 was rather spherical but the shape of alumina is larger than copper, as focused by TEM. The shape of the particles for Cu and Al2O3 was rather spherical but the shape of alumina is larger than copper. On the other hand, the particles of only ZnO showed edges and corners. The crystalline size range was about 2-41 nm.

Figure 4 shows the TPR profiles for Cu-ZnO-Al2O3 catalysts with various preparation methods. The Cu-ZnO-Al2O3 (1:1:8) catalyst starts to reduce below 200 °C, the Cu-ZnO/Al2O3-FSP, with reduction beginning at approximately 260 °C and ending around 380 °C. While reduction of the others catalysts were prepared by solvothermal method and commercial catalyst start at the similar temperature at approximately 235 °C and ending around 270 °C.

Figure 5 shows methanol conversion as a function of temperature on Cu-ZnO-Al2O3 at Cu:ZnO:Al2O3 as 1:1:8 with various preparation methods respectively. The methanol conversion of Cu-ZnO-Al2O3 increase slightly.
Figure 6 shows H$_2$ production rate on Cu-ZnO-Al$_2$O$_3$ catalysts prepared by various methods at Cu-ZnO-Al$_2$O$_3$ as 1:1:8. For H$_2$ production rate, Cu-ZnO/Al$_2$O$_3$-paraffin, Cu-ZnO/Al$_2$O$_3$-butadiol and incorporation by FSP show higher H$_2$ production rate compared with other preparation methods at the same metal/alumina ratio. Moreover, the H$_2$ production rate increases slightly with temperature increase while the H$_2$ production rate of Cu-ZnO/Al$_2$O$_3$-FSP, Cu-ZnO/Al$_2$O$_3$-toluene and Cu-ZnO/Al$_2$O$_3$-com are similar.

Figure 7-8 shows MeOH conversion versus H$_2$ production rate on Cu-ZnO-Al$_2$O$_3$ catalyst with various preparation method respectively. Mostly, hydrogen production rate from methanol have focused on steam reforming and decomposition. Moreover, partial oxidation of methanol and hydrogenation can react at low temperature. At the same conversion, incorporation by FSP shows higher H$_2$ production rate than others preparation method at the same metal/alumina ratio.

Figure 9 shows relative H$_2$ production versus temperature on Cu-ZnO-Al$_2$O$_3$ catalysts prepared by various methods. Relative H$_2$ production based on CO and CO$_2$ production compared with actual H$_2$ production. For relative H$_2$ production with positive values, the catalysts improve partial oxidation of methanol and water-gas shift reaction. For relative H$_2$ production with negative values, the catalysts improve CO (CO$_2$) hydrogenation to cracking products and oxygenated compounds.
4. Conclusions

Incorporation by FSP shows higher H$_2$ production rate. Moreover, the solvothermal catalysts seem to promote the partial oxidation of methanol. The impregnated catalyst improves CO (CO$_2$) hydrogenation and decomposition of methanol to cracking products and oxygenated compounds.

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