

Crystal-Plane Effect of Ceria on the Activity of Cu/CeO₂ for Oxidative Steam Reforming of Methanol

Sivinee Petchakan^a, Apanee Luengnaruemitchai^a, Sujitra Wongkasemjit^a*

^a The Petroleum and Petrochemical College, Chulalongkorn University

Keywords: Copper, Ceria, Oxidative Steam Reforming of Methanol, CuO

ABSTRACT

Oxidative steam reforming of methanol (OSRM) reaction is intensively considered in hydrogen production by using Cu catalysts. Different shapes of ceria (CeO₂) supports, which are single-crystalline and uniform nanorods, nanocubes and mixed-shape of cubic CeO₂, were selectively prepared by a hydrothermal method at temperatures 120 °C, 160 °C and 180 °C, respectively. The CuO/CeO₂ catalysts were prepared by deposition-precipitation method (DP). This research focused on the effect of ceria shape as a support for copper-based catalyst on the catalytic performance and a function of Cu loading in the OSRM reaction. The results show that CuO/CeO₂ exhibit a higher activity the CeO₂ support due to the strong interaction between CuO and ceria. Their activity and selectivity will be evaluated and the catalysts will be characterized by Scanning Electron Microscope (SEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) surface area measurement.

*apanee.l@chula.ac.th

INTRODUCTION

Hydrogen is described as a primary alternative energy in the future by virtue of the fact that it can be produced from both renewable sources such as biomass, solar energy and non-renewable sources (Bičáková and Straka, 2012). Nevertheless, hydrogen can provide clean energy which is environmentally friendly and has gained a considerable interest as an energy carrier useful for various applications and, particularly, for polymer electrolyte membrane fuel cells (PEMFCs) supply (Iulianelli *et al.*, 2014). The ideal fuel for PEMFCs is hydrogen, which shows some limitations regarding storage and transportation. Therefore, to overcome these problems, the in-situ hydrogen generation has made attractive both alcohols and hydrocarbons steam reforming reaction. Methanol became a promising source because it is liquid at ambient conditions, possesses relatively high H/C ratio, low reforming temperature (200-300 °C), easy availability, low contaminant level, safe in handling and it is also producible from biomass (Ahmed and Krumpelt, 2001). In addition, hydrogen can be converted from methanol into hydrogen by several reactions. Steam reforming of methanol (SRM) and partial oxidation of methanol (POM) require heat and produce some CO as a byproduct while oxidative steam reforming of methanol (OSRM) produce only CO₂ as a by-product. Generally, copper-based catalysts are used for the above three reactions due to their high activity and excellent selectivity for CO₂ and H₂ formation. CeO₂ has been used as a support of the copper catalyst for stabilization of the metal dispersion (Udani *et al.*, 2009).

EXPERIMENTAL

A. Catalyst Preparation

1.125 mmol of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 22.5 ml of 6 M NaOH solution were mixed and stirred in a Teflon bottle and then held in a stainless steel autoclave at different temperatures (120 °C for rods; 160 °C for mixed (rods and cubes); 180 °C for cubes) for 24 hours. The suspensions were separated in a centrifuge, dried at 80 °C in a vacuum oven overnight and then calcined at 400 °C for 4 hours. The prepared support (0.1 g) was slurried in 3 ml of DI water. Then a 6 wt% of Cu was added to the above solution dropwise and was stirred for 1 hour. Next, 1 M of Na_2CO_3 solution was added dropwise to the solution and stirred for 1 hour and pH value was kept at 8-10. The obtained precipitates were separated by centrifuge, washed with DI water at 60-70 °C. The precipitates were dried at 80 °C in a vacuum oven overnight, and then were calcined in air at 400 °C for 4 hours (Han *et al.*, 20011).

B. Characterization

Total pore volume, total surface area and average pore diameter of the catalysts were measured by BET analyzer. The crystalline structure of CeO_2 support and the mean particle diameter of copper were analysed by XRD.

C. Catalytic Reaction

The process of oxidative steam reforming of methanol started with the mixture of distilled water and methanol was filled in a syringe before injecting by a syringe pump at a rate of 1.5 ml/hour to an evaporator for making the vapor of methanol and steam. Both methanol vapor and steam were carried by helium, mixed with oxygen stream before entering a catalytic reactor and a flow rate of He and oxygen were varied to keep the constant gas hourly space velocity (GHSV) at 30,000 ml/g-cat hour. The OSRM reaction was carried out in a vertical pyrex glass micro-reactor (9 mm i.d.) at atmospheric pressure using 0.1 g of CuO/CeO_2 in the temperature range from 200 to 400 °C. The effluent gas from the reaction was analyzed by using a gas chromatograph equipped with thermal conductivity detector (TCD).

RESULTS AND DISCUSSION

A. Structural Properties

Fig. 1 shows rod (R), mixed (M) and cubes (C) shapes of the pure ceria supports and CuO/CeO_2 catalysts. The surface area of CeO_2 support were 95.51, 76.78 and 28.72 m^2/g with different shapes (rod, mixed and cube shapes). While the BET surface area of Cu catalysts were 73.25, 42.64, and 27.37 m^2/g . The surface area of CuO/CeO_2 catalysts decreased when compared to CeO_2 support.

The XRD patterns in Fig.2 shows the CuO/CeO_2 catalysts with different shapes (rod, mixed and cube shapes). XRD analysis was employed to investigate the crystalline structure. The characteristic is indexed at (2θ) 28.6°, 33°, 47.5°, 56.4°, 59°, 69.2°, 77° and 79.4°, indicating a cubic fluorite structure of CeO_2 , regarded as the plane indices of (111), (200), (220),

(311), (222), (400), (331) and (420) planes, respectively. It is clearly seen that the XRD patterns exhibit sharper peaks and higher intensity for higher temperature synthesis especially at hydrothermal of 180 °C. In the addition, CuO or Cu peaks were not detected in the CuO/CeO₂ catalysts; it probably due to low concentration of Cu species or the Cu particle size is below the detection limit of XRD technique.

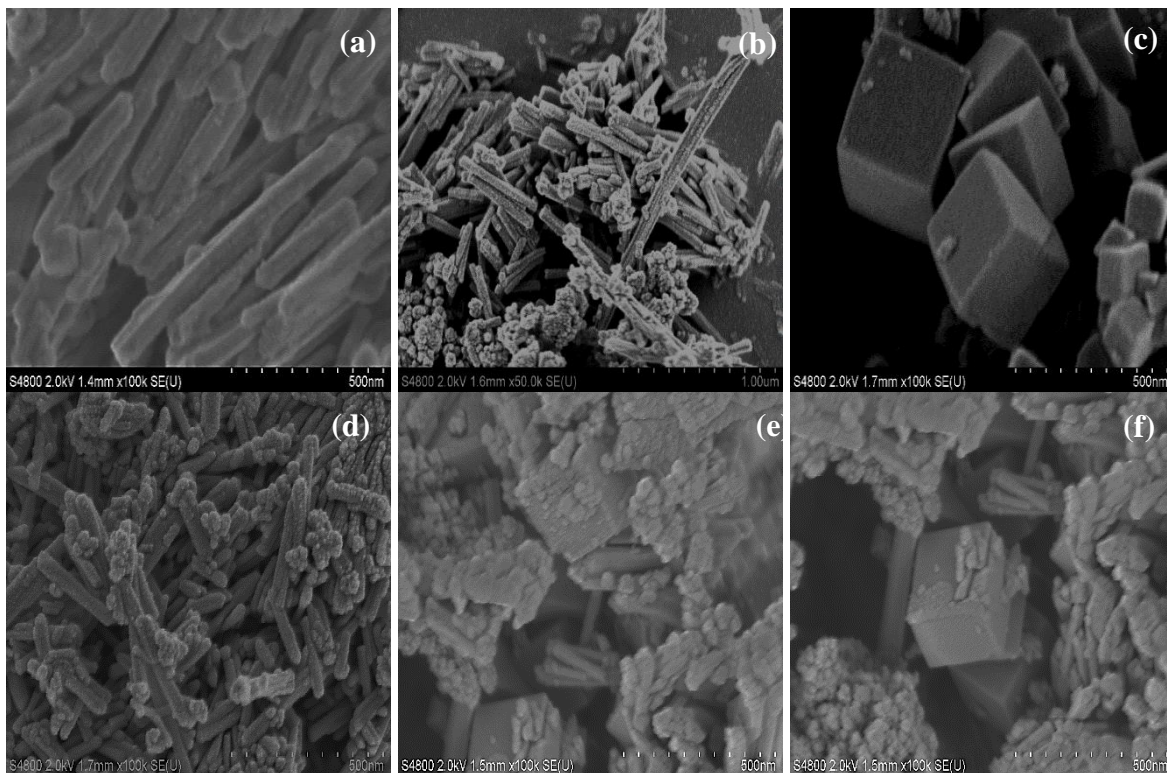


Fig. 1. SEM images of CeO₂ with (a) rod shape, (b) mixed shape, and (c) cube shape and CuO/CeO₂ catalysts with (d) rod shape, (e) mixed shape, and (f) cube shape.

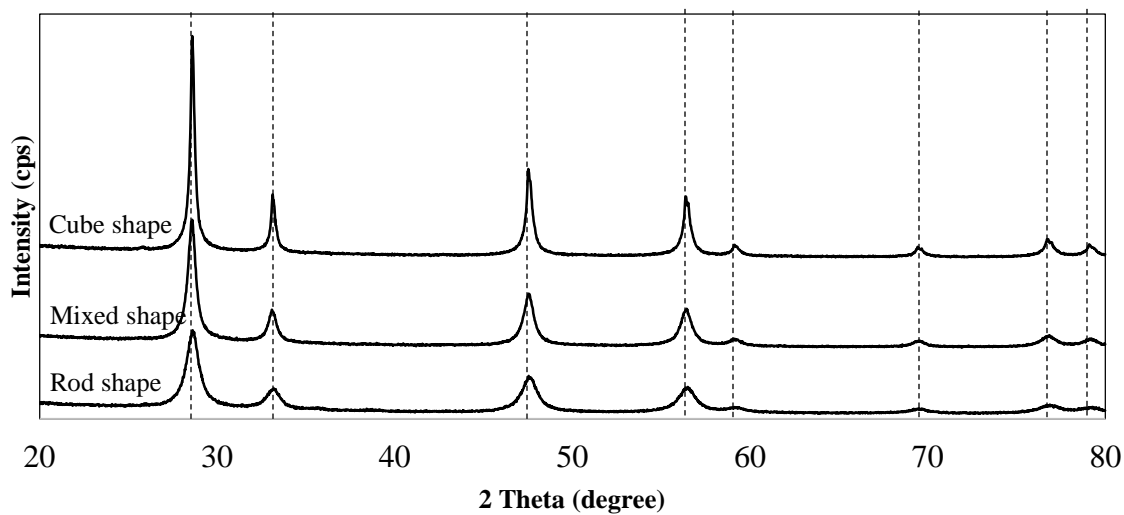
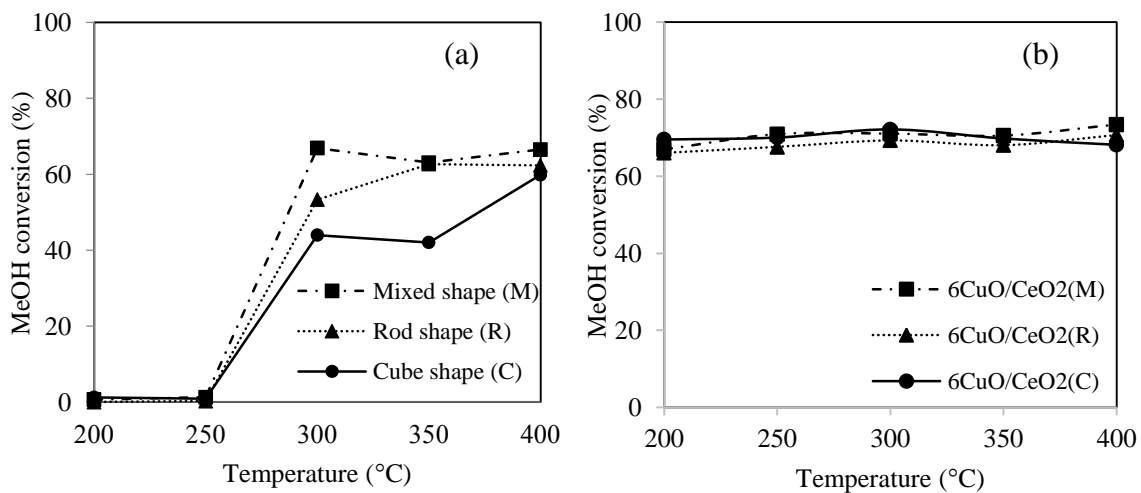


Fig. 2. XRD patterns of the CuO/CeO₂ catalysts with different shapes.

B. Catalytic Performance



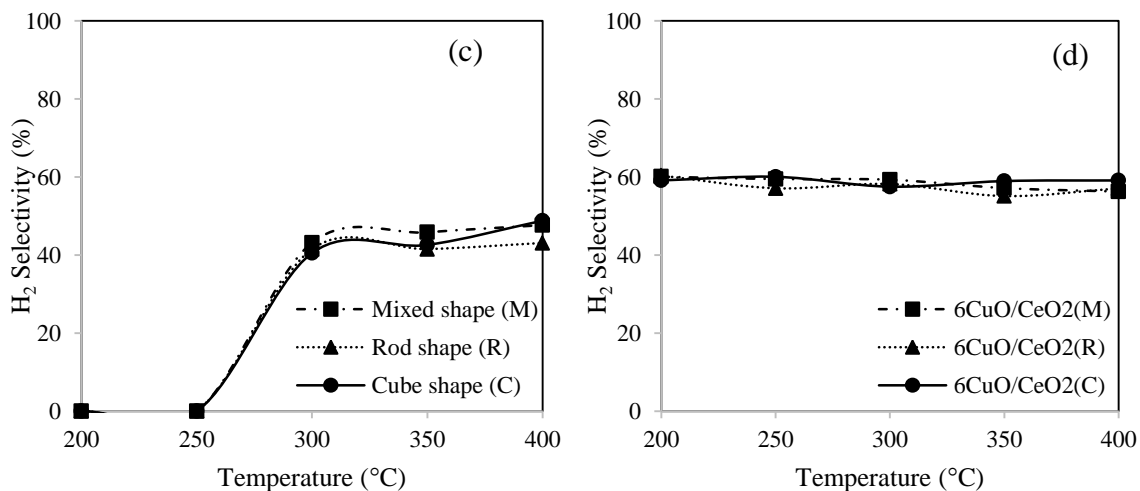


Fig. 3. (a) Conversion and (c) selectivity of the CeO₂ supports and (b) Conversion and (d) selectivity for 6CuO/CeO₂ catalysts.

Fig.3 shows the activity and selectivity for the OSRM reaction. Figs. 3(a) and 3(c) illustrate that the mixed shape of ceria support shows the highest activity about 65%, followed by rod shape and cube shape. However, the highest selectivity is obtained by mixed shape of CeO₂. For CuO/CeO₂ catalysts shown in Fig. 3(b) and 3(d), all of CuO/ceria shows the methanol conversion and the selectivity remain constant at around 70% and 60% all temperature range studied, respectively. From previous result presents the mixed shape of CeO₂ has the best activity and selectivity for OSRM reaction between 300-400 °C while any shapes of 6CuO/CeO₂ catalysts shows high activity in all the time. Not only the shape of catalyst affects the activity and selectivity, but also the metallic copper has significant impact on the activity and selectivity. Whereas, the effect of support has less impact on the activity and selectivity.

CONCLUSIONS

The shape of ceria support affects on the activity and selectivity at high temperatures (≥ 300 °C). The activity and selectivity of the CuO/CeO₂ catalysts are evaluated for OSRM reaction. When copper is deposited on different shapes of ceria (rods, mixed and cubes), the activity and selectivity are higher compared to CeO₂ support due to the strong interaction between CuO and ceria. Moreover, all the activity and selectivity are very similar, the effect of shape of ceria support is not necessary or less importance for the activity and selectivity.

ACKNOWLEDGEMENTS

The author is grateful thanks for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College and the Methee-Vijai-Chula Grant; Grant for International Research Integration.

REFERENCES

- Ahmed, S. and Krumpelt, M.** (2001). *Hydrogen from hydrocarbon fuels for fuel cells*. International Journal of Hydrogen Energy 26(4), 291-301.
- Bičáková, O. and Straka, P.** (2012). *Production of hydrogen from renewable resources and its effectiveness*. International Journal of Hydrogen Energy 37(16), 11563-11578.
- Han, J., Kim, H. J., Yoon, S. and Lee, H.** (2011). *Shape effect of ceria in Cu/ceria catalysts for preferential CO oxidation*. Journal of Molecular Catalysis A: Chemical 335, 82–88.
- Iulianelli, A., Ribeirinha, P., Mendes, A. and Basile, A.** (2014). *Methanol steam reforming for hydrogen generation via conventional and membranereactors: A review*. Renewable and Sustainable Energy Reviews 29, 355–368.
- Jeong, D.-W., Jng, W.-J., Shim, J.O., Han, W./b. and Roh, H.-B.** (2014). *Low-temperature water-gas shift reaction over supported Cu catalysts*. Renewable Energy 65, 102-107.
- Liu, L., Yao, Z. , Deng, Y., Gao, F., Liu, B. and Dong, L.** (2011). *Morphology and Crystal-Plane Effects of Nanoscale Ceria on the Activity of CuO/CeO₂ for NO Reduction by CO*. ChemCatChem 3, 978-989.
- Maciela, C. G., Silvaa, T. de F., Hirookaa, M. I., Belgacemb, M. N. and Assafa, J. M.** (2012). *Effect of nature of ceria support in CuO/CeO₂ catalyst for PROX-CO reaction*. Fuel 97, 245–252.
- Pan, C., Zhang, D. and Shia, L.** (2008). *CTAB assisted hydrothermal synthesis, controlled conversion and CO oxidation properties of CeO₂ nanoplates, nanotubes, and nanorods*. Journal of Solid State Chemistry 181, 1298–1306.
- Udani, P.P.C., Gunawardana, P.V.D.S., Lee, H.-C. and Kim, D.-H.** (2009). *Steam Reforming and oxidative steam reforming of methanol over CuO–CeO₂ catalysts*. International Journal of Hydrogen Energy 34, 7648-7655.
- Zhou, K., Wang, R., Xu, B. and Li, Y.** (2006). *Synthesis, characterization and catalytic properties of CuO nanocrystals with various shapes*. Nanotechnology 17, 3939–3943.