The In-situ XRD Study of Hydrogen Production from Methanol on $Cu_{30}ZnO$ Catalyst

Yuh-Jeen Huang (黃鈺軫)[1,2,3], Ke-Lun Ng (黃科倫)[3], and Hsiao-Yu Huang (黃曉瑜)[2]

[1]Department of Environmental & Safety Englineering,
Chung Hwa University of Medical Technology, Tainan, Taiwan
[2]Department of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan
[3]Department of Biomedical Engineering & Environmental Sciences,
National Tsing Hua University, Hsinchu, Taiwan

The methanol reformer is an excellent substitution for hydrogen high pressure storage tank as a power source for fuel cell. It has the advantages of approximately 4 to 6-folds of power density more than hydrogen high pressure storage tank. Among the methanol reforming reaction, partial oxidation of methanol (POM) can be proceeded at lower temperature without heating as it is an exothermic reaction. The catalyst applied for partial oxidation of methanol (POM) is the $Cu_{30}ZnO$ catalyst. The $Cu_{30}ZnO$ catalyst has the merits of easy to prepare, low cost and good activity [1].

The catalytic activity of $Cu_{30}ZnO$ in POM reaction was shown in Fig. 1. The product of the reaction was hydrogen, carbon dioxide and the by-product was carbon monoxide and steam. The methanol conversion increased from 74 % to almost 100 % and the hydrogen selectivity decreased slightly when the temperature rose to 300 °C. Meanwhile, the carbon monoxide selectivity increased as rising the reaction temperature. It is assumed that, the side reaction, reverse water gas shift reaction, would proceed at the same time resulted in the decrement of hydrogen and increment of carbon monoxide at high temperature (above 225 °C). The equation is shown below:

$$H_2 + CO_2 \rightarrow H_2O + CO \qquad (1)$$

At the same time, the carbon monoxide could come from another reaction [2],

$$CH_3OH + 0.25\ O_2 \rightarrow 0.5\ CO_2 + 0.5\ CO + 2\ H_2 \qquad (2)$$

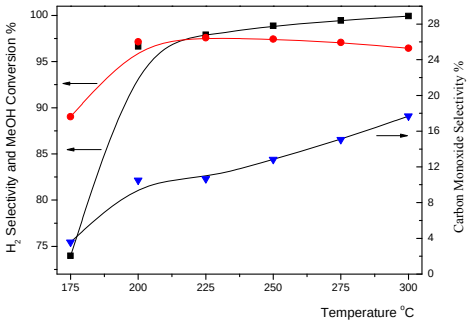

Fig. 1: The temperature profiles of catalytic performances in the POM reaction over $Cu_{30}ZnO$ (■)MeOH conversion (●) Hydrogen selectivity (▼) Carbon monoxide selectivity.

Equation (2) shown that, carbon monoxide is produced without any hydrogen consumed and it could explain as the methanol conversion increased, the carbon monoxide concentration increased but the hydrogen just decreased slightly.

From Fig. 1 we discovered that the catalytic ability is much higher at high temperature, but at lower temperature the catalytic ability dropped sharply. To understand the species transformation, we proceeded the in situ XRD of POM reaction. Figure 2 showed the diffraction pattern of $Cu_{30}ZnO$ catalyst at different reaction temperature. At 300 °C the Cu^0 was found to be the main species in the diffraction pattern, the Cu_2O and CuO showed very weak diffraction. But, at lower temperature the Cu_2O and CuO diffraction peak can clearly seen. It can be explained that Cu^0 initiated the catalytic reaction. From our previous study the Cu_2O was the main intermediate of the reaction, it just shortly appeared and back to Cu^0, so, the diffraction pattern was not obvious at 300 °C. But at lower temperature, the CuO could not reduced back to Cu^0, resulted in the catalytic ability declined.

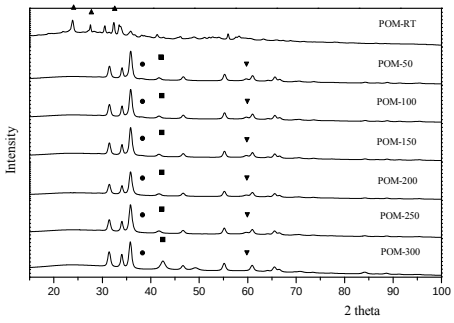

Fig. 2: The in situ XRD of POM reaction at different temperature. ▲Aurichalcite ●CuO ■Cu^0 ▼Cu_2O

From this study, we again confirmed our suggestion that the Cu^0 initiated the catalytic reaction and the formation of Cu_2O was the rate determining step. The catalytic ability declined at low temperature was caused by lack of Cu^0 species to maintain the catalytic properties.

References

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