ZnO Nanowire-supported Ag Catalyst for Methanol Steam Reforming

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Alternative energy sources, such as various fuel cell technologies, have attracted intense attention due to their high efficiency and low emissions of pollutants. Methanol, with its high hydrogen/carbon ratio, low sulfur content and the absence of carbon–carbon bonds, has been identified as a highly suitable source for onboard production of hydrogen [1]. Among several reactions for converting methanol to H₂, methanol steam reforming (MSR) is one of the most attractive processes because it can provide a high H₂ content and an extremely low level of CO in the product [2]. We report here our recent study of Ag nanoparticles (NPs) supported on ZnO nanowires (NWs) as a catalyst for MSR reaction.

ZnO NWs were fabricated by a thermal evaporation-condensation method in a high-temperature tube furnace. The Ag/ZnO nanocatalysts were prepared by a deposition-precipitation method. ZnO NWs were dispersed into deionized water and the suspension was under constant stirring. Then AgNO₃ aqueous solution was added stepwise to the suspension, during which the pH value of the mixture was maintained at a fixed value by adding appropriate amounts of NaOH solution. After filtration and being washed with deionized water, the resultant solid was dried at 60 °C overnight and calcined at 400 °C for 4 hours. The catalyst was reduced by hydrogen at 400 °C for 2 hours, prior to MSR reaction which was conducted in a fixed-bed plug-flow reactor. A mixture of 1.5: 1 moles of water-methanol was pumped using a syringe pump at 0.6 ml h⁻¹. The reaction feed was preheated to 160 °C to vaporize the methanol/water mixture. The JEOL JEM-ARM200F aberration-corrected scanning transmission electron microscope (STEM), with a nominal image resolution of 0.08 nm in the high-angle annular dark-field (HAADF) imaging mode, was used to investigate the structure of the synthesized Ag/ZnO catalysts.

Figure 1a shows a backscattered SEM image of the synthesized 5wt%Ag/ZnO NW catalyst, revealing the general morphology of the ZnO NWs and the presence of some large Ag NPs. Figure 1b displays a low magnification HAADF image of a representative Ag/ZnO NW, revealing small clusters of Ag on the ZnO NW. It is interesting to note that some etch pits (dark patches), often associated with the small Ag clusters, can be clearly seen on the surfaces of the ZnO NW. At high magnifications individual Ag single atoms, located on the positions of the Zn columns, can be clearly observed (indicated by the arrows in Fig. 1c). The stability of these Ag atoms under electron beam irradiation suggests that they may be embedded onto the ZnO surfaces, replacing Zn cations. The performance of the Ag/ZnO NW catalyst was evaluated at different temperatures (Fig. 1d). Pure ZnO NWs, also a catalyst for the MSR reaction, was tested as a control. It should be noted that the Ag/ZnO NW catalyst has a much higher activity and better selectivity toward CO₂ than the pure ZnO NWs. Optimization of the catalyst synthesis processes and applications to other types of catalytic reactions will be discussed [3].

References:

- [1] L. F. Brown, *Int. J. Hydrogen Energy* **26** (2001), p. 381.
- [2] A. Haryanto *et al.*, *Energy & Fuels* **19** (2005), p. 2098.
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Figure 1. Backscattered SEM image of an Ag/ZnO NW catalyst shows some large Ag NPs (a). Aberration-corrected HAADF images of a Ag/ZnO NW (b, c), revealing small Ag clusters, etch pits on the ZnO NW surfaces and isolated individual Ag atoms on the positions of the Zn columns of the ZnO NW. The ZnO NW in Fig. 1c was oriented close to the ZnO [10-10] zone axis. Methanol conversion as a function of reaction temperature on the Ag/ZnO-NW catalyst for MSR reaction (methanol/water (mole ratio): 1/1.5 (0.6 ml/h in liquid), gas hourly space velocity of $\sim 54,000 \text{ ml g}^{-1}_{\text{cat}} \text{ h}^{-1}$). The ZnO NWs were tested as a control.