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Development of Stable Pt_3Zn/ZnO Catalyst by Epitaxial Growth

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Oxides supported metal catalysts are widely used in industrial processes due to their high activity and/or selectivity. The metal particles usually have sizes ranging 1~20 nm to enhance the atomic efficiency. However, when such small metal particles are subjected to chemical reactions at elevated temperatures they may sinter to larger particles, resulting in drop of activity. Therefore, development of thermodynamically stable supported metal/alloy catalysts is highly desirable for practical applications [1]. The stability of oxide-supported catalysts strongly depends on the interaction between the dispersed metal particles and the supports [2]. Epitaxial growth of metal or alloy nanoparticles on metal oxide supports can significantly enhance their interfacial interactions, resulting in strong anchoring of the metal/alloy nanoparticles [3]. In this research, we selected highly stable ZnO nanowires, primarily enclosed by the low-energy {1 0 -1 0} surfaces. The use of such well-controlled single crystal ZnO nanowires has advantages such as homogenous surface structure (compared to powders) and large surface area (compared to large single crystals). We report here our recent progress in synthesizing, characterizing and testing a catalyst primarily consisting of Pt-Zn alloy nanoparticles epitaxially grown on the {1 0 -1 0} surfaces of the ZnO nanowires.

ZnO nanowires were fabricated by a thermal evaporation-condensation method in a high temperature tube furnace. The Pt-Zn/ZnO nanocatalysts were prepared by a deposition-precipitation method. ZnO nanowires were dispersed into deionized water and the suspension was under constant stirring. Then $H_2PtCl_6 \cdot 6H_2O$ 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 Na_2CO_3 solution. After filtration and being washed with deionized water, the resultant solid was dried at 333 K overnight and calcined at 673 K for 4 h in air. Prior to catalytic reaction, the catalysts were reduced at 923K for 2 h in 10% H_2/He. 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 Pt-Zn/ZnO catalysts.

Fig. 1a shows a representative HAADF image of a 2wt% Pt/ZnO nanowire catalyst, revealing the uniform distribution of Pt-Zn nanoparticles (bright dots) across the ZnO nanowires. The average size of nanoparticles was measured to be approximately 3nm in diameter. Figure 1b reveals that all the nanoparticles seem to have aligned with respect to the ZnO {1 0 -1 0} surfaces, resulting in a fixed epitaxial relationship between the nanoparticles and the ZnO nanowires. Detailed analyses of high magnification HAADF images (Fig. 1c) show that the nanoparticles are Pt_3Zn with outer two layers being pure Pt. The Pt_3Zn/Pt core/shell particles grew epitaxially onto the ZnO {10-10} surfaces with an epitaxial relationship as Pt_3Zn (2 0 0) || ZnO (1 -1 0 1) and Pt_3Zn (1 -1 1) || ZnO (1 -1 0 -1). The catalyst was tested using high-temperature water gas shift (HT-WGS) reaction as a probe. To accelerate the sintering effect, a high weight hourly space velocity (WHSV, 57,000 ml/g_{cat}/h v.s. 15,000 ml/g_{cat}/h for the iron oxide-based HT-WGS catalyst) was used. The catalyst was first tested at different temperatures for its rate of conversion (Fig. 2a) and then was tested at 500℃, a temperature higher than the conventional HT-WGS reaction temperature, for about 40 h (Fig. 2b). The excellent stability of the Pt_3Zn/ZnO catalyst is attributed to the epitaxial growth of the Pt_3Zn alloy nanoparticles. Optimization of the catalyst synthesis processes, the control of Pt or Pt_3Zn particle size distributions, and applications of other types of catalytic reactions will be discussed [4].

References

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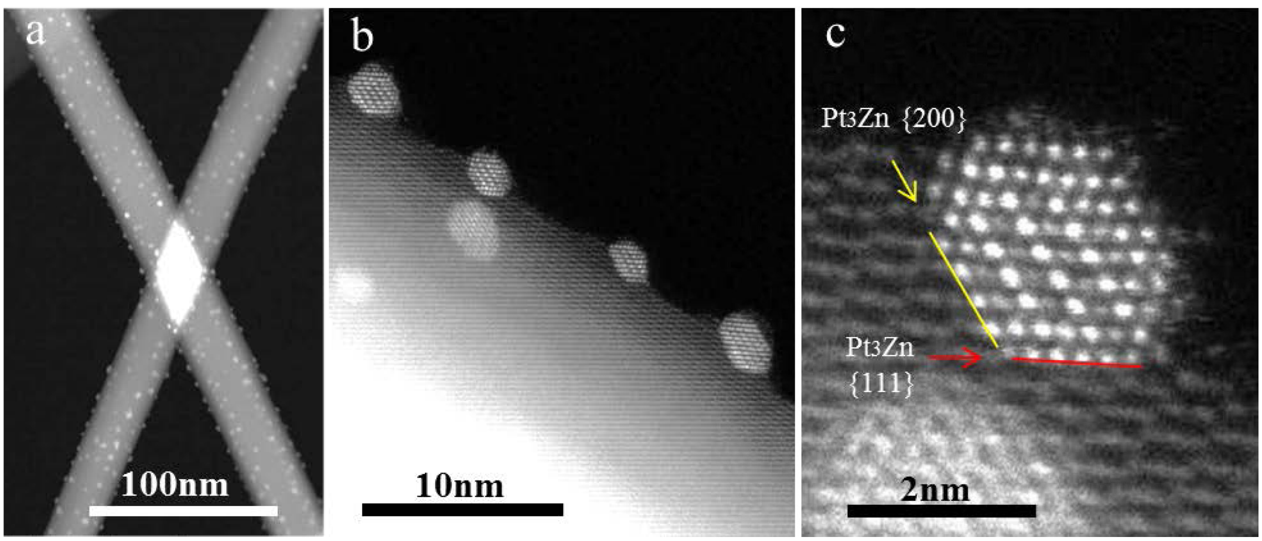

Figure 1. HAADF-STEM images of Pt_3Zn/ZnO nanowire catalyst.

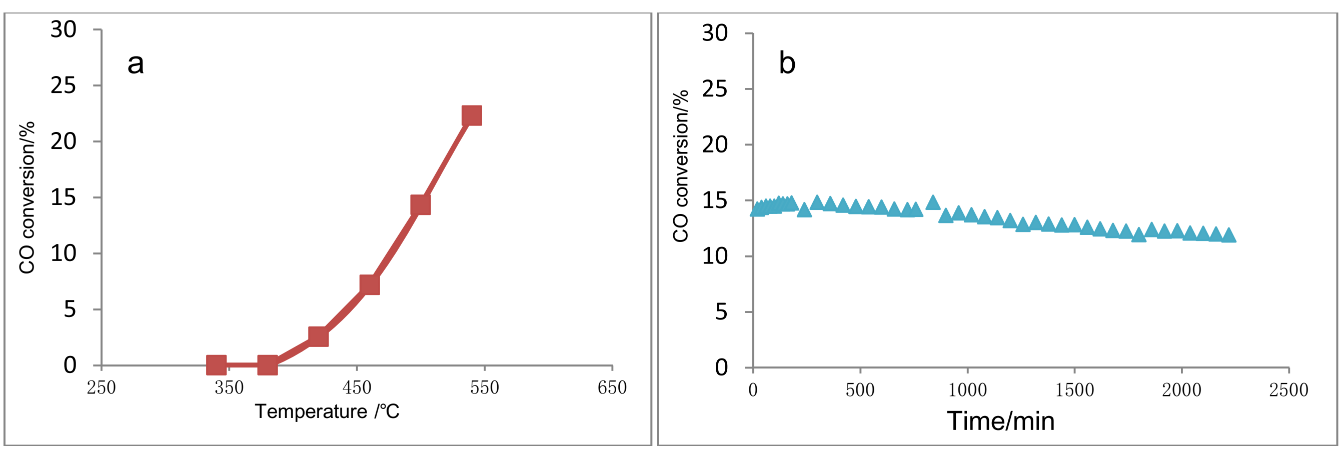

Figure 2. CO conversion as a function of (a) reaction temperature and (b) reaction time at 500℃ on a Pt_3Zn/ZnO catalyst for water-gas-shift reaction. Reaction condition: 2%CO + 10%H_2O, flow rate = 38 ml/min, WHSV = 57,000 ml/g_{cat}/h.