

Faceted ZnO nanowire supported Pd catalyst for the Methanol Steam Reforming

Hongyang Liu* and Jingyue (Jimmy) Liu*,**

* Center for Nanoscience, ** Department of Physics & Astronomy, University of Missouri-St. Louis, One University Boulevard, St. Louis, Missouri 63121

Methanols, due to their easy storage and transport, have been proposed as possible sources of hydrogen. To convert methanol to hydrogen via onboard reforming requires highly active, selective and stable catalysts. Pd supported on ZnO has shown promising properties as a catalyst for onboard steam reforming of methanol to produce hydrogen. And the formation of PdZn alloy nanoparticles has been considered to be responsible for the improved catalytic performance of Pd/ZnO catalysts[1]. However, It has long been suspected that the ZnO support also plays a important role in this reaction[2]. Therefore, in this paper, we reported the study of the faceted ZnO nanowire supported Pd catalyst for the methanol reforming. And try to explore the effect of the ZnO support to the methanol steam reforming.

ZnO nanowire were fabricated by a thermal evaporation-condensation method in a high temperature tube furnace [3]. The deposition of Pd was accomplished by dipping the ZnO nanowires into an aqueous solution containing Pd(NO₃)₂ as precursor salts. The pH value of the aqueous solution was maintained, by adding Na₂CO₃, between 8 and 9. Then filtered, washed and dried at room temperature under vacuum overnight. The nominal Pd loading was 10 wt%. The catalysts was reduced by hydrogen at the temperature of 250 °C for 2 hours, prior to reactivity measurement in methanol steam reforming. Measurements of the steam-reforming of methanol were performed in a tubular packed-bed reactor and 100 mg of catalyst was packed into a reactor consisting of a quartz tube of inner diameter 6 mm. A mixture of 1.1 : 1 moles of water-methanol was pumped using a syringe pump at 0.6 ml h⁻¹.

Fig. 1 showed the work performance of the methanol steam reforming over the ZnO nanowire supported Pd catalysts. We can see that the catalyst exhibited high conversion and high selectivity at the test condition. And the catalyst still kept very stable working ability after 40 hours test (100% of methanol conversion and 97% of CO₂ selectivity), which indicate that it is feasible to use the faceted ZnO nanowire as the support for the methanol steam reforming. Figure 2a and 2b display the XRD results of the Pd/ZnO (nanowire) catalyst before and after methanol steam reforming evaluation, respectively. From the results, we can observe that it can be easily formed PdZn alloy on the support of the faceted ZnO nanowire even reduced by the hydrogen at the temperature of 523 K. And after the methanol steam reforming test, the size of the PdZn alloy particles became bigger around 5-8 nm, compared with the fresh catalyst 2-3 nm. TEM images (Figure 3a and 3b) also displayed that the PdZn alloy particle grow bigger during the process of the methanol steam reforming, which consistent with the XRD results. Meanwhile, the SEM images (figure 4a and 4b) told us that the whole morphology of the ZnO nanowire were well maintained even after the methanol steam reforming reaction. And other structures of ZnO as the support for the methanol steam reforming will also be discussed in the report[4].

References

[1] N. Iwasa, et al. *Appl. Catal. A.* **125** (1995) 145

[2] Z. W. Pan, et al. *Science*. **291** (2001)1947.

[3] A. Karim and A. Datye, *Phys. Chem. Chem. Phys.* **210** (2008) 5584.

[4] This research was funded by the University of Missouri-St. Louis.

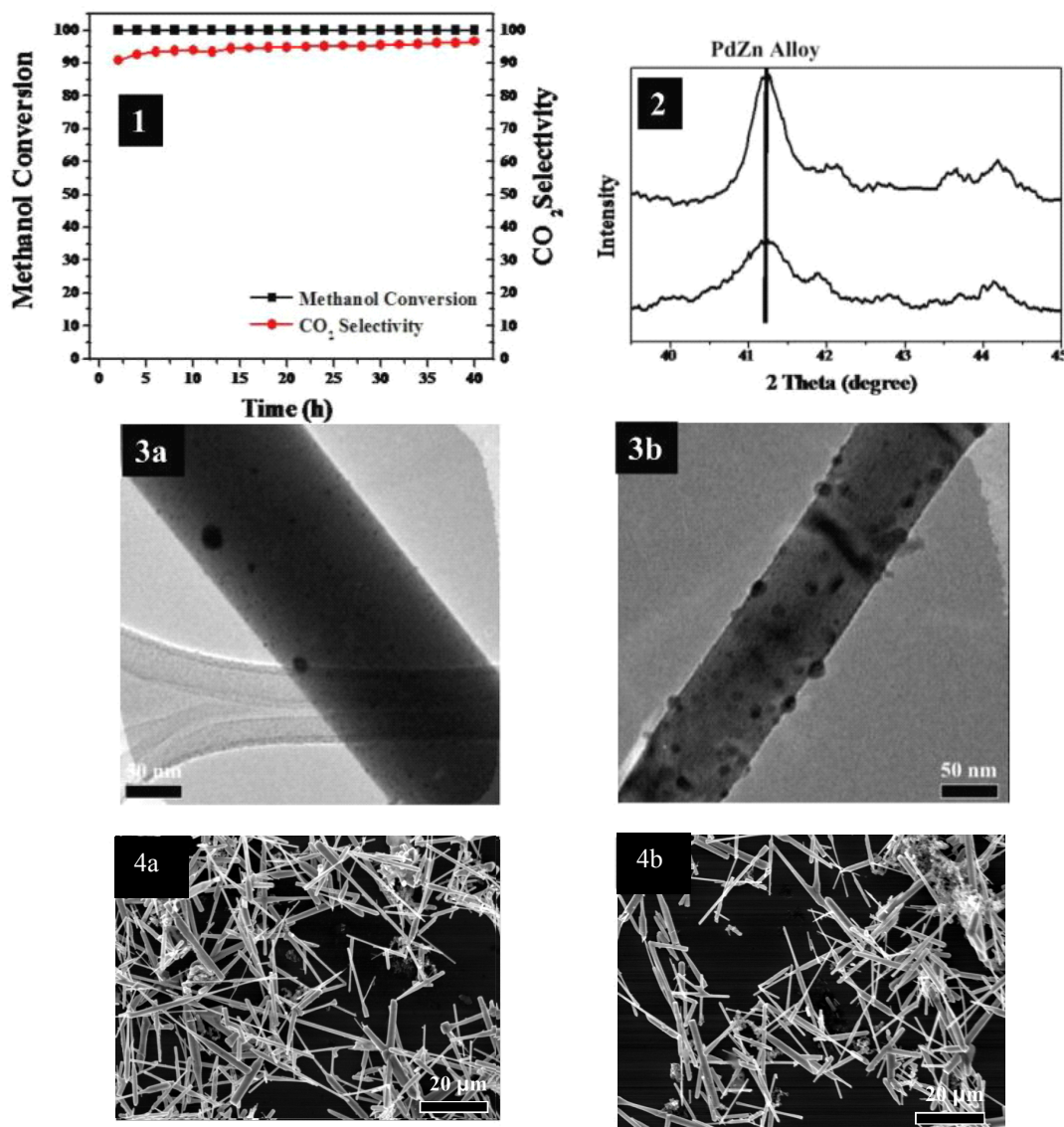


Figure 1 Methanol conversion and selectivity over Pd/ZnO nanowire catalyst. H₂O/CH₃OH molar ratio = 1.1, CO₂ selectivity = moles CO₂/(moles CO + CO₂) × 100, P = 670 Torr, T = 623 K, 100 mg catalyst, 0.6 ml/h

Figure 2 the XRD results of the Pd/ZnO nanowire catalyst before (a) and after (b) the methanol steam reforming evaluation.

Figure 3 TEM images of the Pd/ZnO nanowire catalyst before (a) and after (b) the catalytic evaluation

Figure 4 SEM images of the Pd/ZnO nanowire catalyst before (a) and after (b) the catalytic evaluation