

ZnO-Supported Catalysts for the Steam Reforming of Alcohols

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Introduction

There has recently been a push from the commercial, as well as the military sectors, to develop small fuel cells to serve as mobile power sources to replace lithium-ion batteries in portable electronics [1]. Applications include long-lasting personal power systems for soldiers in the field as well as personal mobile electronics such as laptops. Research has shown that the energy density of small proton-exchange membrane (PEM) fuel cells is several times that of comparable lithium-ion power sources. Hydrogen-fed fuel cells represent a superior design for portable power supplies due to their high efficiency and negligible pollution issues. Therefore, on-demand production of hydrogen from a liquid fuel in a microreactor is much more desirable.

Due to their high energy density and low reforming temperatures, alcohols are often considered the best choice of liquid fuels to generate hydrogen for fueling portable proton-exchange membrane (PEM) fuel cells [2]. However, CO can be an unwanted by-product in the steam reforming of alcohols. Therefore it is important to develop active and selective catalysts towards H₂ and CO₂. Pd/ZnO has been shown in recent years to possess high selectivity towards CO₂ during methanol and ethanol steam reforming [3, 4]. It is commonly assumed that PdZn bulk alloy formation is essential to achieve high selectivity towards CO₂. Co/ZnO is also a well-known catalyst for the steam reforming of ethanol [5], although it has been shown that there is no bulk CoZn alloy formation. In this work, we analyze the effect of the ZnO support on the cobalt and palladium-based catalysts on the steam reforming of alcohols.

Materials and Methods

The catalysts were prepared via impregnation of metal precursors on the metal-oxide supports, followed by calcinations, and subsequent reduction in hydrogen. We used XRD and TEM to obtain estimates of average crystallite size and bulk composition. By using a STEM electron probe of 2.0nm, we can analyze the bulk and surface compositions of these alloy nanoparticles. Measurements of the steam reforming of both alcohols were performed in tubular packed-bed reactors of 1.75mm i.d.. The effluent of the reactors was analyzed using gas chromatography.

Results and Discussion

In the case of methanol reforming, we found that even without any pretreatment, PdZn alloy particles were formed after reaction at 250°C, due to the facile reduction of ZnO in the presence of Pd and H₂. Samples treated at low temperatures in H₂ show the co-existence of monometallic Pd and PdZn alloy particles. On the other hand, high temperature reduction leads complete transformation of Pd to PdZn alloy. However, the selectivity towards CO₂ was found not to increase monotonically with the extent of alloy formation. Samples with low alloy content also showed CO₂ selectivity comparable to those where alloy formation was complete. In each case, lower CO₂ selectivity was exhibited by samples whose average

particle size was around 1.5nm. We conclude that one consequence of high reduction temperatures is to eliminate these small particles via sintering, leading to improved selectivity towards CO₂. We also found that the morphology of the ZnO has an effect on the activity towards steam reforming of alcohols. Specifically, we have performed experiments involving physical mixtures of ZnO with Pd/Al₂O₃, and also ZnO dispersed on alumina. The presence of ZnO leads to enhanced selectivity of CO₂ showing the vital role played by ZnO during the reforming of alcohols.

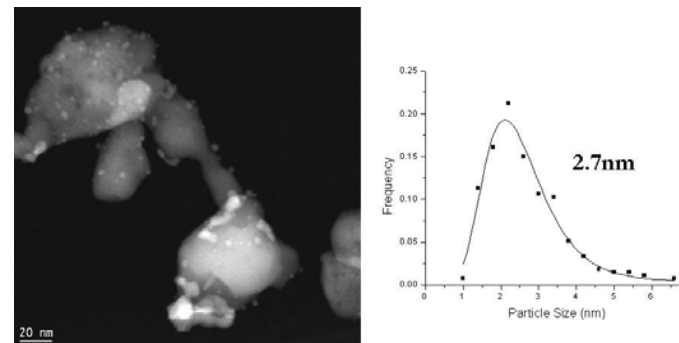


Figure 1: STEM and particles size distribution of the catalyst reduced at 250°C (He ramp). The image was taken after reactivity measurements for four hours. The distribution shows that the average particles size was approximately 2.7nm, and reactivity data showed this catalyst to have a selectivity of 94% selective towards CO₂.

Significance

This study helps to further understand the fundamental role of ZnO in Pd/ZnO and Co/ZnO in the steam reforming of alcohols. We also provide insight into the role of bulk versus surface alloy formation in this catalyst system.

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References

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