

Catalytic Activity and Characterization of Pd/ZnO Catalysts

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Introduction

Steam reforming of methanol has been studied as a source of hydrogen production for the fuel cell due to its high hydrogen/carbon ratio, low sulfur content, and relatively low reforming temperature (250-350°C) [1]. Formation of CO as a by-product should be minimized to avoid deterioration of the fuel cell by CO adsorption. Most studies have been focused on Cu based catalysts which exhibit high selectivity to CO₂ and H₂ [2]. Copper based catalysts, however, have the disadvantages of poor thermal stability above 270°C and pyrophoric characteristic. Group VIII metals are markedly different from the copper catalysts. Over Group VIII metals catalysts methanol decomposes to CO and hydrogen [2]. On the other hand, Iwasa et al were the first to report that Pd supported on ZnO and reduced at >300°C has exceptionally high activity and selectivity to CO₂ and H₂ [3]. The intriguing and promising performances of Pd/ZnO catalysts were attributed to PdZn alloy formation [3, 4]. The small amount of CO over PdZn catalysts in all literature reports was attributed to a small amount of metallic Pd species [4], which may be related to the catalyst preparation. To confirm this hypothesis, we have performed in-situ X-ray absorption spectroscopy (XAS) experiments on the Pd K edge for samples prepared using two different methods.

Methods and Materials

10 wt% Pd/ZnO catalysts were prepared using incipient wetness method. Pd nitrate aqueous solution containing 20 wt% Pd was used to prepare the catalyst labeled as “aqueous preparation”, and Pd acetate dissolved in acetone was used to prepare the catalyst labeled as “organic preparation”. Activity tests were carried out in a 4mm i.d. quartz tube reactor. A SiC to catalyst weight ratio of 5/1 was adopted to ensure isothermal operation. Catalysts were reduced in 10% H₂ at 350°C for two hours before activity testing.

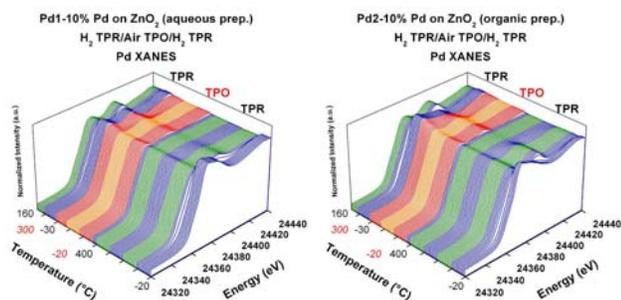


Figure 1. Comparison of XANES data for cyclic TPR/TPO/TPR for 10% Pd on ZnO₂ via aqueous and organic solvent techniques.

Results

In-situ XAS was used to provide insights about the PdZn alloys, ease of Pd reduction, and the presence of metallic Pd. The temperature programmed XANES results using a TPR/TPO/TPR sequence are shown in Figure 1. As can be seen, the Pd laid down using the organic preparation reduces at a lower temperature than the aqueous preparation. The organic preparation is completely reduced by 39°C whereas the aqueous preparation remains in a Pd²⁺ state at temperatures up to ~120°C.

Discussion

EXAFS fitting shows that the as received materials are essentially identical with only the appearance of Pd-O bonding. The Pd sees only oxygen in the first coordination sphere at a distance of 2.01 angstroms. As the catalysts are reduced in hydrogen, Pd-O is reduced to Pd metal with the formation of both Pd-Pd and Pd-Zn bonds. Relatively large metallic alloy particles are produced using both methods, however, the composition of the Pd-Zn alloys are significantly different, with the organic preparation incorporating less Zn (2:1 Pd:Zn ratio compared to 2:3 Pd:Zn ratio for the aqueous preparation). The average Pd-Zn bond length in the alloy is 2.58(2) Å at 100 °C. Further reduction shows little change in these particles.

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References

1. Peters, R.; Dusterwald, H.G.; Hohlein, B., J. Power Sources, 2000, 86, 507.
2. Trimm, D.; Onsan, Z.I., Catal. Rev., 2001, 43 (1&2), 31.
3. Iwasa, N.; Kudo, S.; Takahashi, H.; Masuda, S.; and Takezawa, N. Catal. Lett., 1993, 19, 211.
4. Suwa, Y.; Ito, S.; Kameoka, S.; Tomishige, K.; and Kunimori, K., Appl. Catal. A: General, 2004, 267, 9.

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