Transition Metal Promoters for Pd in Methanol Steam Reforming Applications

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Introduction

A number of emerging applications involving fuel cells require a supply of hydrogen. Catalytic generation of hydrogen is an effective approach, especially since hydrogen storage and refueling present a range of issues [1]. One such approach is the steam reforming of methanol, as shown below.

$$CH_3OH + H_2O \longrightarrow 3H_2 + CO_2$$

In this work, we focused on a series of Pd-based catalysts for the above reaction. The effect of specific transition metals in enhancing the performance of the Pd catalyst was evaluated. In addition to maximizing methanol conversion to hydrogen, another important aspect of this work was to minimize CO formation, which interferes with the operation of the fuel cell [2].

Materials and Methods

The catalyst samples were prepared by incipient wetness impregnation routes. The resulting impregnated powders were calcined in air at 540°C.

The catalyst samples were tested using a micro-channel catalytic reactor. Prior to evaluation, the catalysts were pre-treated in 4% H_2 (balance He) at 400°C for 15 minutes. During the evaluation, a feed stream containing 11.9% methanol, 14.6% water, and a balance of Argon was passed over the sample at various temperatures ranging from 150 to 300°C. The amounts of methanol, H_2, CO_2, and CO in the product stream were measured to determine catalyst performance. The measured CO and CO_2 values were used to calculate the CO_2 selectivity.

Results and Discussion

The first stage of this work focused on the catalyst support. A series of catalysts containing 5% Pd were prepared and tested using a number of supports. The results are summarized in Table 1. The ceria support shows a clear advantage over the other supports in terms of both methanol conversion and selectivity toward CO_2. It should be pointed out that hydrogen formation for these materials corresponded closely with methanol conversion.

Based on the results of the support study, ceria was selected as the support for the second stage of this work, which involved the introduction of secondary metals to the Pd catalyst. Initial studies involving Pd and a second metal, selected among Mn, Fe, and Ni, showed that all three of these metals resulted in some improvement in both methanol conversion and selectivity toward CO_2. Iron and nickel were selected as the more promising candidates.

Table 1. Catalytic Results for 5% Pd Catalysts at 250°C

Support	Methanol Conversion	CO_2 Selectivity *
Ceria	56 %	39 %
Zirconia	22 %	18 %
Titania	23 %	15 %
Alumina	27%	1 %

* CO_2 Selectivity = 100 * CO_2 / (CO + CO_2)

Based on these results, we carried out a systematic study in the Fe-Ni-Pd composition regime. These results are summarized in Figure 1. Nickel-containing catalysts, up to 10% Ni, showed improved methanol conversion with moderate improvement in CO_2 selectivity. Although similar improvement to methanol conversion was observed for Fe-containing catalysts, there was a significant increase in the CO_2 selectivity. The Fe-Ni-Pd combinations did not provide any added advantage. It is important to note that the most preferred Ni-Pd and Fe-Pd compositions were those with the lowest levels of the transition metal.

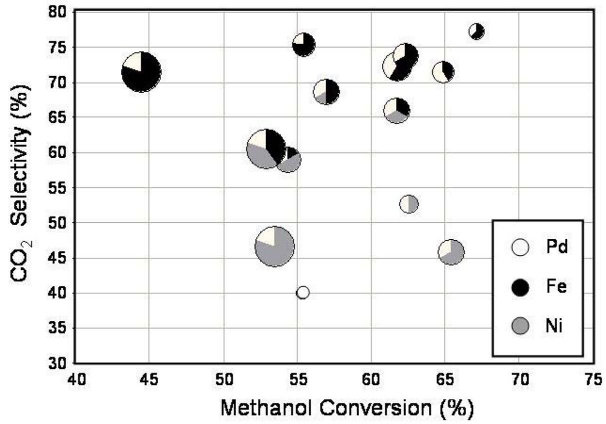

Figure 1. Plot of CO_2 selectivity vs. methanol conversion for the Pd-Fe-Ni composition regime. The size of the circles corresponds to the metal content in the catalyst.

References

1. Larminie, J., and Dicks, S. "Fuel Cell Systems Explained", Wiley, New York, 2000.
2. Shore, L., and Farrauto, R. J. in "Handbook of Fuel Cells: Fundamentals, Technology and Applications" (W. Vielstich, A. Lamm, H. Gasteiger, Eds.), Wiley, New York, 2003.