Oxidative Steam Reforming of Ethanol over Bimetallic PtRu Catalysts

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Introduction

Hydrogen is a multi-function material that used widely as a feedstock in the petrol (hydrotreatment and hydrocracking process), chemical (ammonia and methanol synthesis), food processing (oil and fat hydrogenation), steel and electronics manufacture [1]. Hydrogen can be produced from ethanol through different reforming processes, i.e., steam reforming of ethanol (SRE), partial oxidation of ethanol (POE) and oxidative steam reforming of ethanol (OSRE) [2]. In this work, the OSRE reaction is investigated over supported PtRu catalysts. Six supports (reducible oxides: ZrO_2, CeO_2, Co_3O_4 and irreducible oxides: ZnO, Al_2O_3, NiO) are chosen to prepare bimetallic catalysts. Therefore, the aim of this work centers on developing a very efficient and more stable catalyst for the on-board reforming of ethanol at relatively lower temperatures in order to generate H_2 with high selectivity and low CO in the outlet gas., which will make the down-steam CO clean-up relatively easier for PEMFC applications.

Materials and Methods

Bimetallic PtRu catalysts were prepared by methods of impregnation by using H_2PtCl_6 and $RuCl_3$ as precursors. After drying at 110 °C and calcination under 400 °C for 4 h, prepared samples were crashed to 60 ~ 80 mesh and stored as fresh catalysts. Catalytic activities of prepared samples towards OSRE reaction were tested in a fixed-bed flow reactor at atmospheric pressure (the experimental setup was shown in Fig. 1). Catalyst of 100 mg was placed in a 4 mm i.d. quartz tubular reactor and held by glass-wool plugs. Before reaction, the catalyst was activated by reduction with hydrogen at 200 °C for 3 h.

Results and Discussion

Figures 1and 2 display the C_{EtOH} and distribution of products toward the OSRE reaction over PtRu/CeO_2 and PtRu/ZrO_2 catalysts between 260 and 600 °C. Ethanol is completely converted over the entire temperature ranges. The distribution of H_2 and CO_2 products increases with temperature. The cleavage of the C–C bond is a very important step in the reforming of ethanol. Both platinum and ruthenium can cleave the C–C bond [3, 4]. The distributions are attributable to the almost complete dehydrogenation of ethanol and the slight decarbonylation of acetaldehyde over bimetallic PtRu catalysts. Figures 3 and 4 summarize the Y_{H2} and S_{CO} over bimetallic PtRu catalysts for OSRE reaction under various temperatures. This investigation clearly indicates that the OSRE reaction is more efficient at a lower operating temperature (around 350 °C) for reducible oxide supports (ZrO_2 and CeO_2) mainly a mixture of H_2 and CO_2 with lower distributions toward undesirable CO and CH_3CHO with 100% ethanol conversion. Among these catalysts, the PtRu/ZrO_2 catalyst is an excellent OSRE catalyst of the production of hydrogen at low temperature. The maximum Y_{H_2} is 4.4 and the CO distribution is 3.3 mol % under 340 °C.

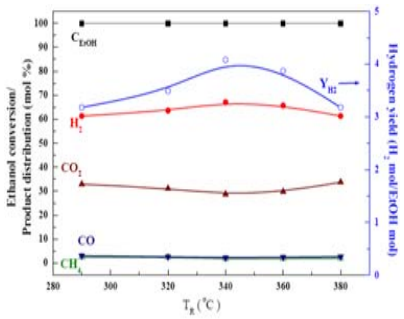

Fig.1 Catalytic performance in the OSRE reaction over PtRu/CeO_2 catalyst

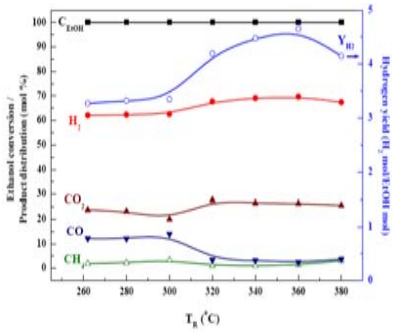

Fig.2 Catalytic performance in the OSRE reaction over PtRu/ZrO_2 catalyst

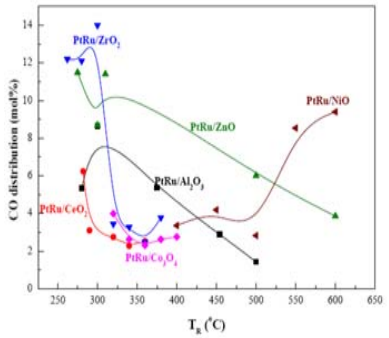

Fig.3 S_{CO} for OSRE reaction under various temperatures

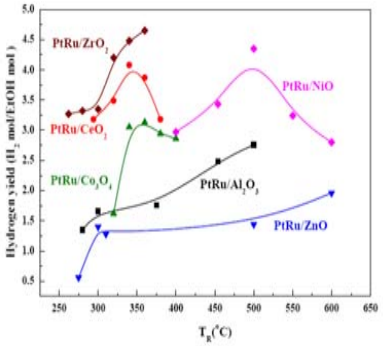

Fig.4 Y_{H2} for OSRE reaction under various temperatures

References

1. Ramachandran, R., and Menon, R.K. Int. J. Hydrogen Energy 23, 593 (1998).
2. Bi, J.L., Hong, Y.Y., Lee, C.C., Yeh, C.T., and Wang, C.B. Catal. Today 129, 322 (2007).
3. Davda, R.R., Shabaker, J.W., Huber, G.W., Cortright, R.D., and Dumesic, J.A. Appl. Catal. B: Environmental 56, 171 (2005).
4. Lee, A.F., Gawthrope, D.E., Hart N.J., and Wilson, K. Surf. Science 548, 200 (2004).