

Selective CO Removal in a Hydrogen-Rich Stream over CuO-CeO₂ and Ni/YSZ

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Introduction

The selective CO removal in a hydrogen-rich stream has been considered to be essential in a fuel processor for the polymer electrolyte membrane fuel cell (PEMFC) because even small amounts of CO can degrade the electrochemical performance of Pt-based anode [1]. The acceptable CO concentration is below 100 ppm even at CO-tolerant alloy electrode [2]. Although various methods such as a membrane separation, the preferential CO oxidation (PROX), and the selective CO methanation [3] have been examined, the PROX has been regarded to be most promising. In the PROX, the catalyst active for the selective CO oxidation in the presence of excess hydrogen is essential. A number of PROX catalysts such as CoO, CuO-CeO₂, supported noble metal (Au, Pt, Rh, and Ru) catalysts have been reported [2]. In the case of transition metal oxide catalysts, the presence of water and CO₂ in the hydrogen stream has an adverse effect on the catalytic activity. Furthermore, these catalysts have a rather narrow temperature window showing high CO conversions. On the other hand, the supported noble metal catalysts have been reported to have a rather wide reaction temperature window exhibiting high CO conversions to meet the CO concentration level for the PEMFC. In the previous work [4], we proposed the double bed system composed of CuO-CeO₂ active for the PROX and Ni/YSZ active for the CO methanation to meet the requirement for the PEMFC feed through only non-noble metal catalysts. In this report, some results related to the performance of this system with different reaction parameters are presented.

Materials and Methods

The CuO-CeO₂ catalyst was prepared by the co-precipitation method as described in the previous work [5]. The Cu content was intended to be 8wt%. This CuO-CeO₂ catalyst was calcined in air at 973 K before a reaction. A Ni/Y-ZrO₂ catalyst was prepared by a conventional wet impregnation method from Ni(NO₃)₂ and Y-ZrO₂ (TZ-8YS, Tosoh). The Ni content was intended to be 10 wt%. This Ni/Y-ZrO₂ was calcined in air at 773 K and reduced in the hydrogen stream at 773 K before a reaction.

Catalytic activity tests for PROX were carried out in a small fixed bed reactor with catalysts composed of 1g of CuO-CeO₂ and 4g of Ni/YSZ. A reactant gas flow was fed to a reactor at an atmospheric pressure. The effluent gas composition was determined through an online gas analyzer (NGA2000, MLT4, Rosemount Analyzer System from Emerson Process Management) of each gas component (CO at ppm level, CO₂, H₂, CH₄ at % level).

Results and Discussion

The single CuO-CeO₂ catalyst cannot decrease the CO concentration from 1 vol% to below 100 ppm in the practical condition through the PROX. In the case of Ni/YSZ, the effluent CO concentration cannot be decreased to below 20 ppm when the initial CO concentration is higher than 2000ppm. Therefore, each catalyst cannot be applied to the CO removal system before the PEMFC. However, the double bed system composed of CuO-CeO₂ and Ni/YSZ connected in series can remove CO almost completely even in the presence of excess H₂, H₂O, and CO₂ as shown in Fig. 1. Furthermore, we can decrease the O₂ concentration to be stoichiometric for CO oxidation. The CO methanation performed over Ni/YSZ should be responsible for the further removal of CO as revealed by the formation of CH₄.

Significance

The almost complete CO removal in the presence of excess hydrogen, water and CO₂ can be accomplished by non-noble metal catalysts (CuO-CeO₂ and Ni/YSZ) over a wide reaction temperature, which is essential to the hydrogen production from hydrocarbons for the PEMFC.

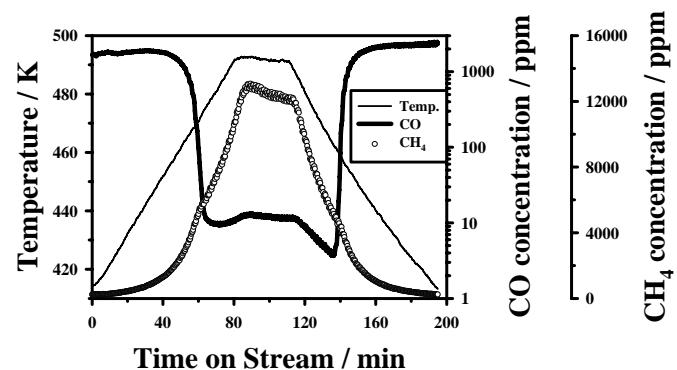


Figure 1. The effluent concentrations of CO and CH₄ based on the dry gas composition after the preferential CO oxidation over the double bed system (CuO-CeO₂ and Ni/Y-ZrO₂) with increasing reaction temperatures at a ramping rate of 1 K/min. Reactants: 0.9% CO, 0.45% O₂, 17.4% CO₂, 64.6% H₂, 13.0% H₂O, balanced with N₂, F/W=69ml/min/g_{cat}.

References

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