Preferential CO Oxidation over Supported Ru Catalysts

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Introduction

The polymer electrolyte membrane fuel cell (PEMFC), in which H_2 is utilized as a fuel to produce H_2O as an end product, has recently attracted much attention as a small-scale power generation system [1]. The H_2 production is currently carried out in a fuel processor in which various hydrocarbons can be converted into H_2 and CO_2 via steam reforming and water-gas shift reaction [1]. Because the latter reaction is thermodynamically limited, a small amount of CO can be present in the H_2 stream and this can cause the degradation of electrochemical performance of Pt-based anode of PEMFC. Therefore, the further purification process is in need to meet the purity of hydrogen for this PEMFC. Until now, several methods including the membrane separation as well as the catalytic removal have been disclosed [2]. Among them, the preferential CO oxidation (PROX) in which CO can be selectively oxidized with O_2 in the presence of H_2, has been intensively studied [2]. Although a number of catalysts have been reported to be active for this reaction [2], supported noble metal (Pt [3, 4] and Ru [5]) catalysts have been generally considered to be promising. In the case of supported Ru catalysts, only a few works have been reported compared with lots works on Pt-based catalysts for this reaction. In this work, we have found that the kinds of support can strongly affect the PROX activity over supported Ru catalysts.

Materials and Methods

All the catalysts were prepared by a wet-impregnation method from an aqueous Ru nitrosyl nitrate solution and different supports such as yttria-stabilized zirconia (YSZ, TOSOH), TiO_2 (P25, Degussa), SiO_2 (Aldrich) and γ-Al_2O_3 (Alfa). All the catalysts were reduced in H_2 at 573 K before a reaction.

For activity comparison, a standard gas of 1.0 vol.% CO, 1.0 vol.% O_2, 50 vol.% H_2, 20 vol.% CO_2 and 2 vol.% H_2O balanced with He was fed to the reactor at an atmospheric pressure. The conversion of CO and O_2 was calculated from the ratio of the consumed amount to the initial amount of each gas. The CH_4 yield was determined by the ratio of the produced CH_4 amount to the initial CO amount. Finally, the CO_2 selectivity for the PROX was defined as the ratio of the consumed O_2 amount in CO oxidation to the total amount of consumed O_2.

CO chemisorption, O_2 chemisorption, a temperature-programmed reduction (TPR) with H_2 and a temperature-programmed oxidation (TPO) with O_2 were conducted to characterize catalysts.

Results and Discussion

The PROX activity with a function of reaction temperature was measured over Ru catalysts supported on different supports such as YSZ, TiO_2, SiO_2 and γ-Al_2O_3 as shown in Fig. 1. Ru/YSZ showed the high CO conversion at low temperatures. The low temperature PROX activity decreased in the order: Ru/YSZ > Ru/TiO_2 > Ru/SiO_2 > Ru/γ-Al_2O_3. Ru/YSZ also exhibited the maximum CO conversion for all reaction temperatures among tested supported Ru catalysts. Ru/YSZ was also determined to be the most active for CO methanation followed by Ru/TiO_2. Compared with other supported Ru catalysts, Ru/YSZ was found to accommodate the large amount of O_2 based on the O_2 chemisorption. The presence of easily reducible oxygen can be confirmed for Ru/YSZ with H_2-TPR after the O_2 chemisorption. These peculiar properties can lead Ru/YSZ to be active for PROX at low temperatures.

Significance

The preferential CO oxidation over supported Ru catalyst was strongly dependent on the kinds of support. Ru/YSZ showed the highest low-temperature PROX activity and also showed the maximum CO conversion among tested catalysts. This high PROX activity appeared to be related to facile O_2 activation.

Figure 1. CO and O_2 conversion, CH_4 yield and CO_2 selectivity with a function of reaction temperature over supported Ru catalysts. F/W = 1,000 ml/$g_{cat.}$/min.
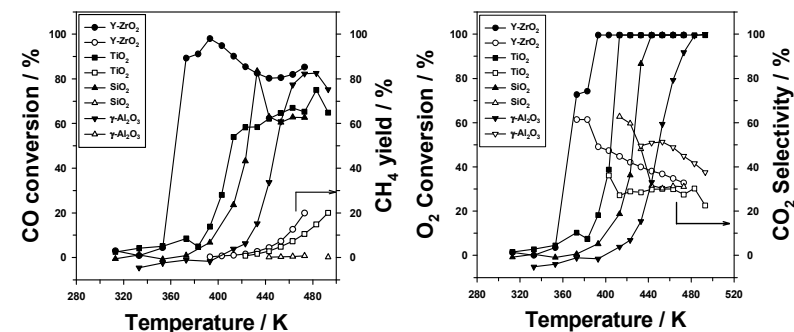
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