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Selective CO oxidation with real methanol reformate over monolithic Pt group catalysts: PEMFC applications

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Abstract

Alumina supported Pt group metal monolithic catalysts were investigated for selective oxidation of CO in hydrogen-rich methanol reforming gas for proton exchange membrane fuel cell (PEMFC) applications. The results are described and discussed in the present paper and show that $Pt/\gamma Al_2O_3$ was the most promising candidate to selectively oxidize CO from an amount of about 1 vol% to less than 100 ppm. We have investigated the effect of the O_2 to CO feed ratio, the feed concentration of CO, the presence of H_2O and/or CO_2, and the space velocity on the activity, selectivity and stability of Pt/Al_2O_3 monolithic catalysts. Afterwards, the Pt/Al_2O_3 catalyst was scaled up and applied in 5 kW hydrogen producing systems based on methanol steam reforming and autothermal reforming. The hydrogen produced was then used as fuel for an integrated PEMFC.

Keywords: PEMFC; Selective CO oxidation; PROX; Hydrogen purification

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are regarded as the most promising candidates for mobile and stationary power applications due to their novel characteristics of high efficiency and low emissions [1–5]. CO-free hydrogen is an ideal fuel for PEMFCs. If no large capacity hydrogen storage systems are available, hydrogen can be produced from methanol, methane, gasoline or other hydrocarbon fuels via steam reforming, partial oxidation or autothermal reforming with a subsequent water-gas-shift (WGS) reaction [5,6]. A typical dry reformate contains about 40–75 vol% H_2, 15–25 vol% CO_2, 0–20 vol% N_2 and 1 vol% CO. Under the operating temperatures of PEMFCs, trace amounts of CO will poison the anode due to strong CO chemisorption on the Pt-sites, and will thus lower the performance remarkably. Therefore, the CO concentration in the reformate has to be reduced to less than 100 ppm for a conventional PtRu-anode of PEMFCs [7–9].

Mainly, there are four methods to reduce CO down to the 100 ppm level: (1) adsorption purification; (2) palladium-based membrane purification; (3) catalytic CO methanation; and (4) selective CO oxidation.

Adsorption purification requires unacceptably large volumes of adsorbents. The palladium-based membrane separation is costly and the operation temperature of Pd membranes lies in between 350 and 500 °C. Catalytic CO methanation consumes 3 mol of H_2 to convert one mol of CO, and there are about 20 vol% CO_2, which can potentially react with H_2 and would thus consume large amounts of the desired product. Accordingly, selective CO oxidation is considered as the most promising and cheap method [3,10].

So far, supported Pt or promoted Pt group metals have been proposed for CO preferential oxidation (PROX) in H_2-rich gases [3–6,10–23] and it seems that supported Pt group metals can be effective for selectively oxidizing CO to the 100 ppm level. Oxide-supported gold catalysts (Au/MeO_x)

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have also been investigated for this purpose. The performance of Au/MeO_x strongly depends on the support and the size of the Au crystallites [24–28]. Recently, Cu-based catalysts have been reported to be effective for selectively oxidizing CO in H_2-rich gases [9,29–34]. However, relatively few publications are available on this reaction for the operation of PEMFCs under real conditions, and practical applications of the catalysts are seldom reported up to now.

In this study, four monolithic catalysts, i.e. Pt, Pd, Rh and Ru catalysts supported on cordierite monoliths coated with γ-Al_2O_3, were investigated for selectively oxidizing CO with O_2 under conditions similar to PEMFCs operations. The Pt/Al_2O_3 catalyst was found to give the best results in terms of PROX of CO, i.e. showing the highest CO activity and selectivity towards CO_2. A $0.5\%Pt/Al_2O_3$ monolithic catalyst could selectively oxidize a feed concentration of 1 vol% CO to less than 100 ppm in a single-stage reactor by adding 1 vol% O_2 into the reformate. The performance of the Pt/Al_2O_3 catalyst was very stable in a 1000-h durability test. Conclusively, this catalyst has been successfully applied in 5 kW methanol reforming systems.

2. Experiment

2.1. Catalyst preparation

Pt, Pd, Rh and Ru monolithic catalysts were prepared by the impregnation method. At first, a γ-Al_2O_3 slurry was coated onto the cordierite monoliths (400 cells/inch, supplied by Corning Corporation), dried in a microwave for 5 min, and then calcined in a muffle furnace at 500 °C for 2 h. The γ-Al_2O_3 coated monoliths were then impregnated with Pt, Pd, Rh and Ru precursor solutions, respectively. After that they were dried in a microwave for 5 min, and then calcined in a muffle furnace at 500 °C for 2 h. The noble metal loadings were about 0.5%. Before the tests, the monolithic catalysts were reduced in a pure hydrogen flow at 450 °C for 3 h.

2.2. Reactor system

The catalytic oxidation of CO was carried out under atmospheric pressure in a quartz tubular reactor (15 mm inner diameter). The samples were fixed in the tube using quartz wool. A K-type thermocouple was affixed to the outer wall of the tube and the tip is parallel to the catalyst top to control the reaction temperature. Fig. 1 shows the experimental setup. It should be mentioned that this setup allowed one to adjust the feed temperature but did not ensure isothermal reaction conditions. The experimental results will therefore show a pronounced light-off behavior of the combustion reaction if the oxygen feed concentration is sufficiently high and the light-off temperature is exceeded. The adiabatic temperature rise of the reaction is 140 °C if 1 vol% O_2 is burned to equal amounts of CO_2 and water. Because the experiment was not carried out at adiabatic condition, and the actual temperature rise along the catalyst bed was about 70 °C.

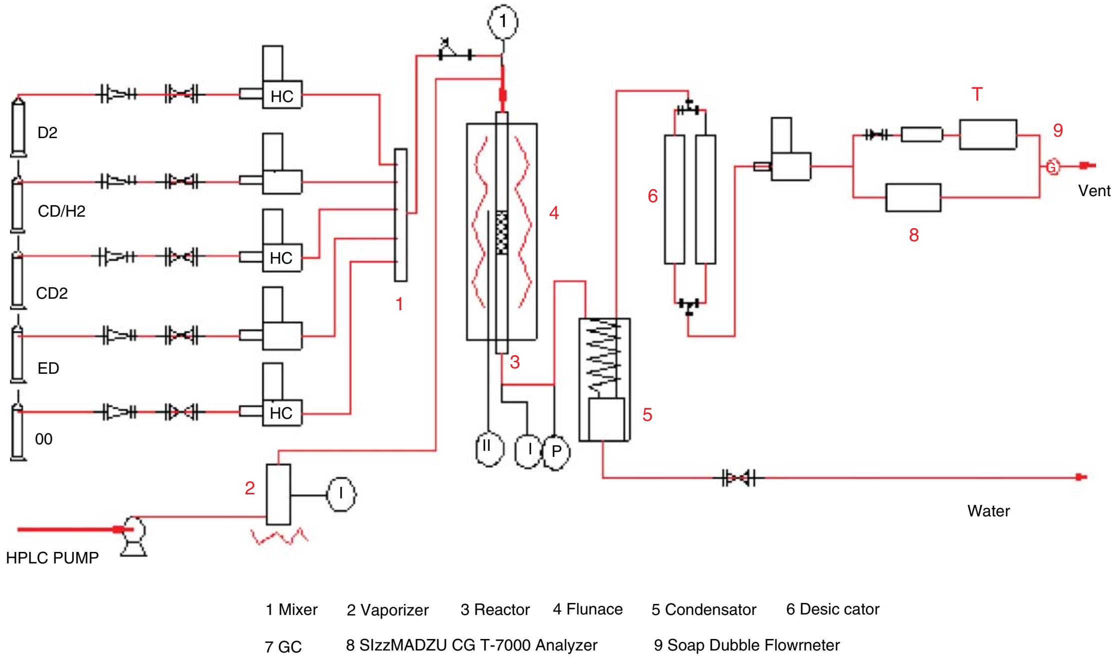

Fig. 1. Experimental setup for the selective CO oxidation in H_2-rich reformate from methanol reforming.