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Performance of catalysts CuO-ZnO-Al$_2$O$_3$, CuO-ZnO-Al$_2$O$_3$-Pt-Rh, and Pt-Rh in a small reformer for hydrogen generation

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Abstract

This study experimentally investigates the performances of catalysts CuO-ZnO-Al$_2$O$_3$, CuO-ZnO-Al$_2$O$_3$-Pt-Rh, and Pt-Rh in a reformer designed to generate hydrogen from a solution of methanol and water for proton exchange membrane (PEM) fuel cell. The results show that both of the methanol conversion and the hydrogen yield rates increase with temperature. For the three catalysts tested, catalyst CuO-ZnO-Al$_2$O$_3$ provides the best performance at temperatures lower than 320 °C. However, at higher temperatures, the performance of this catalyst deteriorates, while that of CuO-ZnO-Al$_2$O$_3$-Pt-Rh and Pt-Rh continue to improve. It suggests that the addition of Pt and Rh to the original CuO-ZnO-Al$_2$O$_3$ catalyst has a stabilizing effect upon the reforming process under higher temperature conditions. The results also show that a higher methanol feed rate reduces the methanol conversion rate, but increases the hydrogen yield rate. It is found that both of the methanol conversion and the hydrogen yield rates reduce as the steam-to-methanol ratio is increased. Finally, the performance can be significantly improved by introducing a turbulence inducer upstream of the catalyst carrier and by increasing both the length and the cell density of the honeycomb structure.
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Keywords: Proton exchange membrane fuel cell; Reformer; Methanol–steam reforming reaction; Catalyst; Conversion rate; Yield rate

1. Introduction

Hydrogen is a highly efficient fuel source for proton exchange membrane (PEM) fuel cells. However, difficulties arise in its storage, filling and transportation. These difficulties can be overcome to a large extent by the in situ generation of hydrogen from other chemicals via a reforming process using appropriate catalysts. Of the various reactants considered for such applications, methanol is regarded as one of the most suitable [1–3].

In general, the design of the reforming system used to generate hydrogen gas is dependent on the specific application for which the hydrogen gas is required. For example, various reforming systems comprising a reformer unit, a catalytic burner and a gas conditioner have been constructed for use in PEM fuel cells designed for automobile applications [4–13]. In [6], Emonts added a catalytic burner to the exit of the nozzle and heat unit to reduce the H$_2$O, CO$_2$, CH$_3$OH and CO contents of the fuel. A compact plate-fin reformer (PFR) has been stud-

ied in the literature [14,15]. Edwards et al. [16] built a hot spot methanol processor capable of producing 750 L of hydrogen per hour from a reactor with a volume of 245 cm^3 and a cold start-up time of just 50 s. Reformer units with built-in palladium membranes to provide ultra-pure hydrogen gas were built and tested [10,11,17–21]. Horng [22] investigated the cold start transient characteristics of a small methanol reformer for a fuel cell. Kumar et al. [23] and Ahmed et al. [24] used an ultrasonic nozzle to achieve a rapid mixture for the solution of methanol and water.

In 2002, Holladay et al. [25] presented a novel miniature reformer system for micro fuel cell applications, in which both the reformer and the combustor had a volume of less than 5 mm^3. Subsequently, various study groups proposed alternative mini- and micro-steam reformers characterized by high surface to volume ratios [26–37]. However, these micro reformers generally suffered the disadvantages of high cost and the undesirable ingress of the catalyst powder into the micro-channels of the fuel cell.

Methanol–steam reforming is traditionally performed using CuO-ZnO as a catalyst. However, this catalyst suffers a number of limitations, including poor stability, a restricted life, and a

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Nomenclature

C	concentration of products (%)
L	length of catalyst carrier (mm)
$\dot{m}$	methanol feed rate (mole min^{-1})
N	honeycomb cell density (cell in.$^{-2}$) (CPSI)
SV	space velocity (h^{-1})
T	temperature of catalytic reaction (°C)
Y	hydrogen yield rate (mole min^{-1})

Greek letters

α	steam-to-methanol ratio (mole mole^{-1})
β	methanol conversion rate (%)

Fig. 1. Schematic illustration of current test system.

limited high-temperature performance. In [17,38,39], the authors reported that these problems could be resolved to a certain extent via the addition of alumina. Furthermore, Nakamura [40] demonstrated that the addition of a noble metal into the catalyst improved its performance at 400 °C, SV = 5 h^{-1}, and $\alpha = 2$. However, neither amount nor component of the noble metal was mentioned in this work.

Despite the notable contributions of the studies presented above, some points remain to be clarified regarding the optimal reforming system for the generation of hydrogen gas for portable fuel cells via a methanol–steam reforming process. Accordingly, the present study performs a series of experimental investigations to determine the performance of three different catalysts, i.e. CuO-ZnO-Al$_2$O$_3$, CuO-ZnO-Al$_2$O$_3$-Pt-Rh and Pt-Rh, under various operating conditions and different reformer unit designs. The study shows the catalytic characteristics of Pt and Rh, which were not investigated for the application in the methanol reforming reaction.

2. Experimentation

The performances of CuO-ZnO-Al$_2$O$_3$, CuO-ZnO-Al$_2$O$_3$-Pt-Rh and Pt-Rh were investigated using the experimental system shown in Fig. 1. The core component of the test system was the reactor unit itself. This unit was made of SCM21 alloy steel and had a length and internal diameter of 145 and 26 mm, respectively. The reactor unit was specifically designed in such a way that it could be easily assembled, dismantled and maintained. Conceptually, the reactor unit could be divided into three separate regions, where each region corresponded to a particular stage of the reforming process. The first region was the turbulence region, located at the entrance of the reactor unit and contained the turbulence inducer shown in Fig. 2. On entering the reactor unit, the reactants were forced to flow within the crosshatched slots machined into the outer rim of the inducer and therefore left the inducer with a high degree of turbulence. The gases then entered the second region of the reactor unit, namely the buffer region, and became thoroughly mixed as a result of turbulence mixing mechanisms. Finally, the mixed gases flowed through the heated catalyst carrier (the third region) and were reformed into hydrogen and various other reaction products.
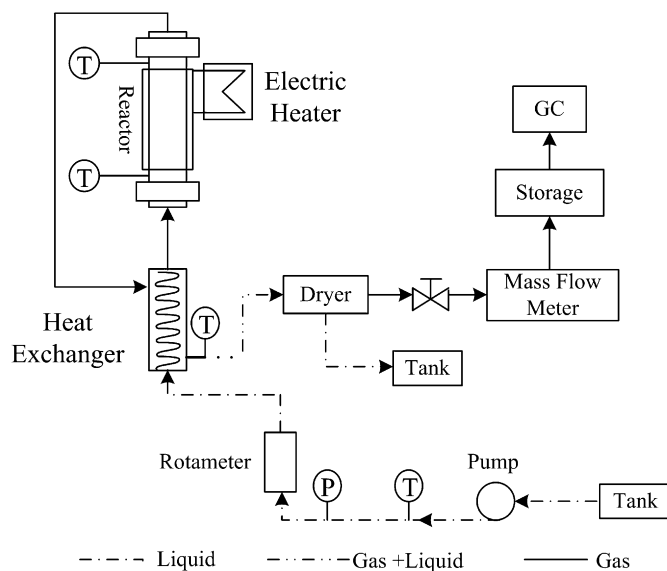
As shown in Fig. 3, the catalyst carriers were fabricated with honeycomb structures of different densities. The carriers were manufactured from stainless steel and were designed with a diameter of 23.4 mm such that they would fit tightly within the reactor unit. To investigate the effect of the carrier length on the reaction performance, the carriers were fabricated in two different lengths, i.e. 40 and 65 mm, respectively, such that total carrier lengths of 40, 65, 80 and 105 mm could be obtained by arranging suitable combinations of carriers end-to-end within the reactor unit. The honeycomb structures within the catalyst carriers were constructed with densities of 200, 300 and 400 cells per square inch (CPSI) of cross-sectional area. The surfaces of these cells were coated with a thin layer of the catalyst of interest, i.e. CuO-ZnO-Al$_2$O$_3$, CuO-ZnO-Al$_2$O$_3$-Pt-Rh or Pt-Rh. The compositional details of these three catalysts are summarized in Table 1. The catalysts were prepared by the impregnation method. The catalyst carrier was, at first, immersed in the aqueous solution of catalyst. Then the carrier was dried in an oven at 105 °C for 24 h and calcined in air in a sintering furnace at 450 °C for 4 h. Finally, aluminum oxide (γ-Al$_2$O$_3$) was coated on the carrier to increase the adherence of catalysts. Note that for convenience, the catalysts are denoted simply by A, B and C, respectively. In catalysts A and B, the catalytic effect was produced primarily by the CuO and ZnO components, and the Al$_2$O$_3$ component was included mainly to enhance the adherence of the catalyst to the stainless steel surfaces of the honeycomb cells. Catalysts A and B were distinguished by the addition of the noble metals Pt and Rh to the latter. These metals were added to catalyst A to prevent the well-known deterioration in the performance of CuO and ZnO under high-temperature conditions. Catalyst C, containing only the noble metals Pt and Rh, was included in the current experiments simply to investigate the relative effectiveness of different types of catalyst.

As shown in Fig. 1, the test system also included a fuel tank, a pump, a rotameter, a heat exchanger, an electric heater with a power of 550 W, a dryer, a pressure regulator valve, and vari-