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A diesel fuel processor for stable operation of solid oxide fuel cells system: I. Introduction to post-reforming for the diesel fuel processor

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ABSTRACT

In this paper, a new concept of diesel fuel processing is introduced for the stable operation of solid oxide fuel cells (SOFCs). High temperature operation of SOFCs can lead to the capability of internal reforming with fuel flexibility. SOFCs can directly use CH_4 and CO as fuels given sufficient steam feeds due to catalytic reaction on the SOFC anode. However, heavier hydrocarbons than CH_4, such as ethylene, ethane, propane, etc., induce carbon deposition on the Ni-based anode of SOFCs. In the case of an ethylene steam reforming reaction on the Ni-based catalyst, the rate of carbon deposition is faster than it is when hydrocarbons, including aromatics, are used. Hence, the removal of light hydrocarbons (over C_1-hydrocarbons), especially ethylene, with the reformate gases of heavy hydrocarbons (diesel, gasoline, kerosene, and JP-8) is important for stable operation of SOFCs. A new methodology, called the "post-reformer", is introduced for removing the light hydrocarbons (over C_1-hydrocarbons) with the reformate gas stream. The CGO-Ru (3.0 wt.%) catalyst was selected as the post-reforming catalyst because it shows high selectivity for removing light hydrocarbons (over C_1-hydrocarbons) and achieving the high reforming efficiency. The diesel reformer and post-reformer are continuously operated for about 200 h in an integrated mode. The reforming performance did not degrade, and light hydrocarbons (over C_1-hydrocarbons) in the diesel reformate were completely removed.

1. Introduction

Due to global warming issues and the depletion of fossil fuels, fuel cells are receiving increased attention as electrochemical conversion devices [1,2]. Fuel cells are classified according to their operating temperature. Typical examples of high temperature fuel cells and low temperature fuel cells are the solid oxide fuel cell (SOFC) and the polymer electrolyte membrane fuel cell (PEMFC), respectively. Each type of fuel cell has its particular advantages. SOFCs have some merits due to the high operating temperatures, such as high system efficiency and fuel flexibility. Fuel flexibility, which is one in strong points of SOFCs, is essential in the application of the fuel cell system. The operation of the SOFCs does not rely on pure hydrogen as a fuel, but may also use carbon monoxide and light hydrocarbons [3,4]. The anode material of the SOFCs can internally reform CO and CH_4 into hydrogen due to its capability to steam reform (SR) [Eq. (1)] and catalyze the water-gas shift (WGS) [Eq. (2)] reactions [5]. It is possible that a wide range of fuels, including natural gas (NG), liquefied petroleum gas (LPG), and liquid hydrocarbon fuels, can be used by the SOFCs system.

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

Although the diesel reformate contains higher concentrations of light hydrocarbons (CH_4, C_2H_4, C_3H_8, etc.) than other hydrocarbons (NG and LPG) reformate, diesel has attracted considerable attention as a hydrogen source for the SOFC system. The attraction of diesel fuels is due to the fuel flexibility of SOFCs and the merits of diesel reforming [4]. For hydrogen production, diesel has some advantages, such as high hydrogen density and existing refueling infrastructure. Diesel reforming also poses several problems. These include the high content of light hydrocarbons (over C_1-hydrocarbons) in the reformate, the occurrence of carbon deposition, the poisoning of reforming catalysts by sulfur, and difficulties in delivering diesel fuel to the reforming reactors. Among the several reforming methods available (i.e., steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR)), ATR is the most appropriate for guaranteeing long-term performance because it minimizes carbon deposition in diesel reforming [6–9]. However, the ATR reformate still contains the light hydrocarbons

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(over C_1-hydrocarbons) in the ATR product gas, which induces carbon deposition on the Ni-based anode of the SOFCs.

Theoretically, it is possible for the SOFC anode to use the hydrocarbons. In our previous research, we found that SOFCs could directly use CH_4 as a fuel given sufficient steam feeds. Methane can be internally reformed very well by an electrochemical reaction on the anode of the SOFC at $H_2O/CH_4 \geq 1.5$ [10]. However, catastrophic performance degradation of the SOFC is induced by the supply of the C_2H_4 or normal-C_4H_{10} as a fuel at $H_2O/CH_4 \geq 1.5$ [11]. Rostrup-Nielsen et al. identified C_2H_4 as a severe carbon precursor to rapid carbon deposition on the Ni-based catalyst during the SR reaction [12]. The catalytic SR reaction of hydrocarbons on the Ni-based catalyst is similar to the reaction of the reformate that includes the light hydrocarbons on the Ni-based anode of SOFCs. Ethylene in the reformate causes rapid carbon deposition on the anode of the SOFCs [13]. Carbon deposition from light hydrocarbons (especially C_2H_4) in the reformate is an important issue that must be suppressed to guarantee stable operation of the SOFC system. The ethylene concentration is higher than the concentration of other hydrocarbons in the diesel reformate, and the ethylene concentration in the reformate clearly increases with decreasing reforming performance in diesel reforming [6,14,15]. It is necessary to remove all hydrocarbons except the CH_4 in the diesel reformate for suppression of carbon deposition on the anode of the SOFC.

In this paper, a new concept for diesel fuel processing, called "post-reforming", is introduced for removing the light hydrocarbons (over C_1-hydrocarbons) with the reformate gas stream. The objective, the decomposition of light hydrocarbons (over C_1-hydrocarbons), of both post-reforming and pre-reforming is the same [16,17]. However, the temperature of the post-reforming reaction is slightly higher than that for the pre-reforming reaction. Generally, the range of pre-reforming temperatures is from 300 °C to 500 °C. In a self-sustaining diesel ATR, the temperature of reformate is about 450–600 °C, so the temperature of the post-reforming reaction is in this range.

The commercial catalyst (Ni-based catalyst) of pre-reforming was used for post-reforming tests, but the Ni-based catalyst exhibited some problems, such as the need to use hydrogen for the reduction process and the ease of carbon deposition over the Ni catalyst. Hence, several novel metal catalysts were tested to select an effective catalyst for post-reforming. Finally, a commercial diesel ATR was operated with a post-reforming process.

2. Experimental

2.1. Microreactor test

A schematic diagram of the microreactor used in this study for the diesel ATR with the post-reforming reaction is shown in Fig. 1. The reactants for the diesel ATR are fuel, water, and air. The reformate of the diesel ATR is supplied directly to the post-reformer. In the case of the post-reforming catalyst test, the diesel ATR reactions were carried out at an O_2/C ratio = 0.5 and a $H_2O/C = 2$, with a synthetic fuel feed. Our previous research has shown that synthetic diesel I, a mixture of n-$C_{12}H_{26}$ and $C_{11}H_{10}$ (n-$C_{12}H_{26}$: 70 vol%; $C_{11}H_{10}$: 30 vol%), is in a good agreement of performance with commercial diesel [6]. After each catalyst test, both ATR and post-reforming microreactors were changed to new microreactors. In the case of the long-term performance test, the reaction was carried out at an O_2/C ratio = 0.8 and a $H_2O/C = 3$, with a commercial diesel (GS-caltex, Korea) feed for comparison to previous research results [6]. The fuel and de-ionized water (>15 MΩ) were supplied by an HPLC (high performance liquid chromatography) pump (MOLEH Co. Ltd.). The air and N_2 were regulated using a mass flow controller (MKS Co. Ltd.). The ATR and post-reforming reactors were made from a 12.7 mm STS (stainless steel) tube and placed inside an electrical furnace to maintain the reforming temperature. A gas hourly space velocity (GHSV) of 12,500 h^{-1} was selected, and the temperature of the electrical furnace was set at 800 °C for the ATR reaction. The post-reforming test was performed at a variety of reaction temperatures on various catalysts. The reaction conditions of all experiments are indicated in each figure caption.

2.2. Catalysts

The ATR reforming catalyst of Pt on Gd-doped CeO_2 (CGO-Pt) used in this study is a noble metal-based catalyst [18]. For the post-reforming test, a conventional pre-reforming catalyst (C11-PR from Süd-Chemie) was first obtained in the form of pellets, and then several catalysts, such as CGO-Pt (0.5 wt.%), CGO-Ru (0.5 or

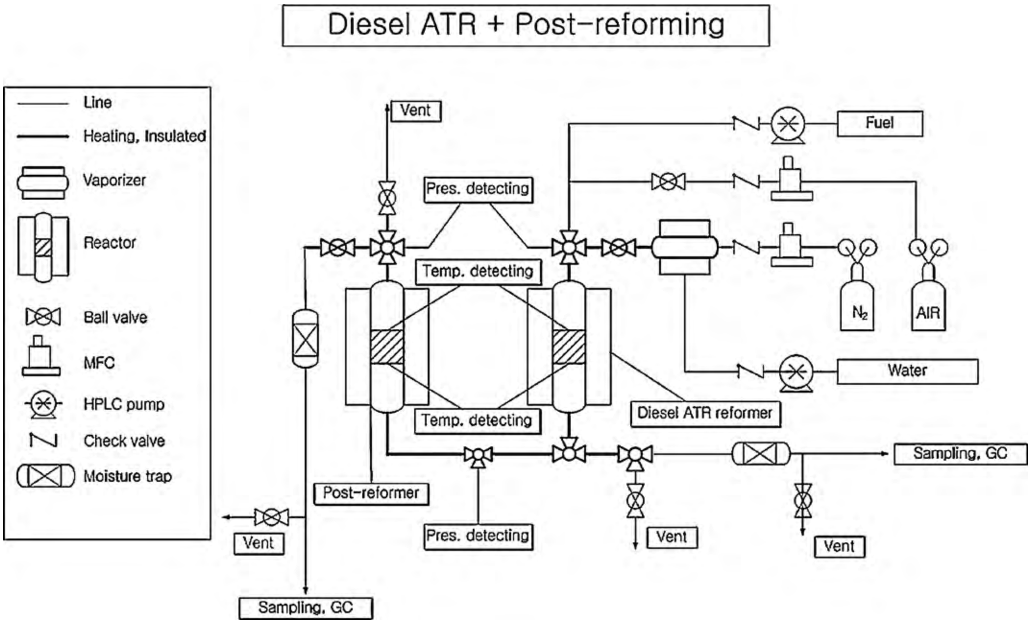

Fig. 1. Schematic diagram of the microreactor system.