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Development of *iso*-octane fuel processor system for fuel cell applications

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ABSTRACT

An *iso*-octane fuel processor system with three different reaction stages, autothermal reforming (ATR) reaction of *iso*-octane, high temperature shift (HTS) and low temperature shift (LTS) reactions, was developed for applications in a fuel cell system. Catalytic properties of the prepared Ni/Fe/MgO/Al_2O_3 and Pt–Ni/CeO_2 or molybdenum carbide catalysts were compared to those of commercial NiO/CaO/Al_2O_3 and Cu/Zn/Al_2O_3 catalysts for ATR and LTS reaction, respectively. It was found that the prepared catalysts formulations in the fuel processor system were more active than those of the commercial catalysts. As the exit gas of *iso*-octane ATR over the Ni/Fe/MgO/Al_2O_3 catalyst was passed through Fe_3O_4–Cr_2O_3 catalyst for HTS and Mo_2C or Pt–Ni/CeO_2 catalyst for LTS reaction, the concentration of CO in hydrogen-rich stream was reduced to less than 2400 ppm. The results suggest that the *iso*-octane fuel processor system with prepared catalysts can be applied to PEMFC system when a preferential partial oxidation reaction is added to KIST *iso*-octane reformer system.

1. Introduction

Hydrogen is the ideal fuel for the stationary and auxiliary fuel cell-powered units as well as a proton exchanged membrane (PEM) fuel cell. Recently, PEM fuel cells operating with H_2 from steam reforming or partial oxidation of hydrocarbon are being increasingly accepted as the most appropriate power source for future generation vehicles. The successful development of a fuel cell-powered vehicle or of stationary fuel cell-powered units is dependent on the development of a fuel processor [1,2].

A direct hydrogen system has many disadvantages such as the lack of widespread refueling infrastructure and high storage volume compared to the hydrocarbon based fuels such as methanol and gasoline. It is known that methanol yields the highest vehicle efficiencies among all the available liquid fuels [1–3]. However, gasoline is the best candidate fuel for the fuel cell-powered vehicle, because the lower efficiency of gasoline in comparison with methanol can be compensated by its much higher energy density compared to methanol and also by its well developed infrastructure [2,3].

Major process technologies for reforming hydrocarbons and alcohols into hydrogen, carbon monoxide and carbon dioxide are catalytic steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR) [2–4]. Steam-reforming reaction of hydrocarbon usually takes place at temperature around 700 °C at which it shows the highest reforming efficiency. But the drawback is that this reaction is an endothermic and therefore, the reactor needs to be heated by combustion of fuels itself. Recently, the results of an investigation carried out to develop sulfur-tolerant reforming catalyst were reported [5–7]. However, no sulfur tolerant steam-reforming catalyst has been designed especially in the presence of high sulfur-containing fuel feeds, resulting in need of a very efficient and therefore probably large unit for removing the sulfur contained in fuels [2,5–7]. POX and ATR systems do not require external heating and can be heated up internally relatively quickly by exothermic reaction of fuels. Hence they are more dynamic than steam-reforming system. The sulfur tolerance for ATR system is also better than that of steam reforming. Also, the ATR process attracts much attention primarily due to the low energy requirement, the opposite contribution of the exothermic hydrocarbon oxidation, endothermic steam-reforming reaction and also due to the high space velocity compared to the POX process [8].

The water gas shift (WGS) reaction is one of the key catalytic stages in a fuel processor. Its function is to reduce the carbon monoxide concentration, at the same time increasing hydrogen content. Since the reaction is an exothermic, the equilibrium CO conversion is highest at low temperature. Consequently, a two-stage process is often used [9–11]. In industrial reactors, Fe_3O_4–Cr_2O_3 and Cu–Zn/Al_2O_3 catalysts are used for the high temperature shift (HTS) and for the low temperature shift (LTS) reactions, respectively. The reaction is moderately exothermic with $\Delta H = -41.1$ kJ/mol [10]. The water gas shift reaction is usually carried out in two adiabatic shift reactors, the high temperature

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shift reactor and the low temperature shift reactor, separated by an intercooler in between. In our previous work, we have reported [12–15] the development of a gasoline fuel processor including ATR over a commercial ICI reforming catalyst, high temperature water gas shift reaction over Fe_3O_4–Cr_2O_3 catalyst and low temperature shift reaction over $Cu/ZnO/Al_2O_3$ catalyst. We have pointed out the necessity of development of high performance, coke and sulfur-resistant ATR and LTS catalysts, the various experimental features of the gasoline processor as well as the goals to be achieved in the near future.

In present study, we have selected *iso*-octane, a principal constituent in gasoline as a fuel feed. So the results obtained over *iso*-octane feed can be used to develop an *iso*-octane fuel processor system. We have carried out the ATR reaction of *iso*-octane, high temperature water gas shift reaction and low temperature shift reaction, and developed the *iso*-octane fuel processor system with three different reaction stages for integration with PEM fuel cell and SOFC based systems. *iso*-Octane fuel processor system charged with prepared catalyst was compared with those charged with commercial ATR and LTS catalysts, respectively.

2. Experimental

2.1. Chemical

The *iso*-octane as a fuel source was supplied by J.T. Baker. The standard *iso*-octane feed containing 100 ppm of sulfur was prepared by mixing of requisite amount of thiophene (99%+, Acros Organics) to *iso*-octane. Hydrogen (99.999%), air (99.999%) and nitrogen (99.999%) were used in the reaction and for the pretreatment of catalysts. Nickel nitrate, ferric nitrate, ammonium molybdate and magnesium hydrate were procured from Sigma–Aldrich Co. Also, γ-alumina (2–3 μm) was obtained from High Purity Chemicals.

2.2. Catalysts

The commercial ATR catalyst ($NiO/CaO/Al_2O_3$) for *iso*-octane reforming, HTS (Fe_3O_4–Cr_2O_3) and LTS ($Cu/ZnO/Al_2O_3$) catalysts for clean up of CO were obtained from ICI in the form of pellets. However, all catalysts in this work were pressed, crushed and particles with a mesh size of 120/230 were selected for the reaction.

The KIST ATR ($Ni/Fe/MgO/Al_2O_3$) catalyst was prepared by the method of incipient wetness of the γ-alumina with aqueous solutions of the corresponding metal nitrates [12,13]. Molybdenum carbide catalyst was synthesized by the temperature-programmed carburization method of molybdenum oxide [16–18]. Pt–Ni/CeO_2 catalyst was prepared by incipient wetness method.

2.3. Catalyst characterization

BET surface area and total pore volume of catalysts before and after the reaction of *iso*-octane were measured by N_2 physisorption. Active metal surface area of catalyst was calculated by CO chemisorption using a sorption analyzer (Quantachrome Co., Autosorb-1C). Structure of the catalysts before and after the reaction was analyzed by a XRD analyzer (Shimazdu Co., XRD-6000).

2.4. iso-Octane fuel processor system

The schematic diagram of an *iso*-octane fuel processor system is shown in Fig. 1. Also, Fig. 2 shows a photograph of *iso*-octane fuel processor system designed by KIST. It consists of six sections: feed supply, evaporator, ATR reactor, HTS reactor, LTS reactor and GC analysis sections. The gases were delivered by mass flow controllers, whereas, H_2O and liquid fuels were fed by liquid delivery pumps (Young Lin Co., model M930). Both evaporator and ATR reactor were made up of an Inconel 600 tube (0.0095-m i.d. and 0.20-m length), HTS and LTS reactors made up of Inconel 600 tube (0.0075-m i.d. and 0.20-m length) were employed in this study. The temperature of evaporator, ATR, HTS and LTS reactors was controlled by a PID temperature controller and was monitored by a separate thermocouple placed in the catalyst bed. This arrangement was capable of ensuring the accuracy of ±1 °C of the catalyst bed temperature. Unreacted H_2O was removed by an ice trap and then gas effluent was analyzed by on-line GC.

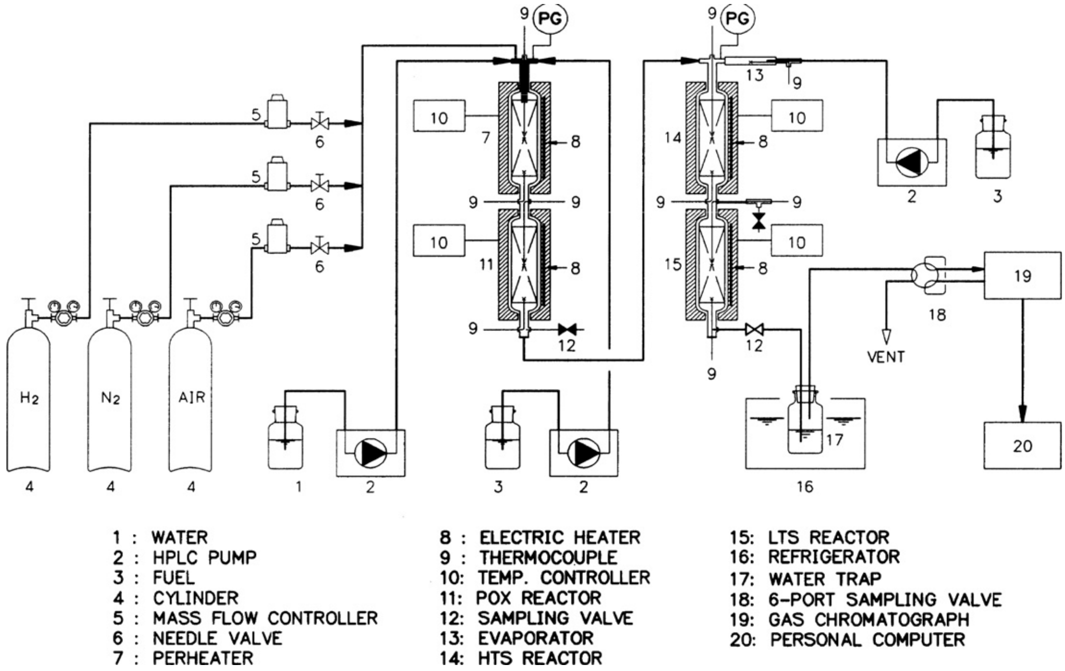

Fig. 1. A schematic diagram of *iso*-octane fuel processor system.