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Exhaust gas fuel reforming for hydrogen production with CGO-based precious metal catalysts

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HIGHLIGHTS

- CGO-based precious metal catalysts are investigated for exhaust gas reforming.
- Iso-octane and commercial gasoline primary test was investigated with Pt/CGO.
- For lower temperature operation, Me/CGO catalysts were investigated. (Me = Pt, Rh, Ru).
- Ru/CGO catalysts show better catalytic reforming performance at lower temperature, around 600 °C.

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ABSTRACT

This paper investigated the fuel reforming of exhaust gases with Me/$Ce_{0.9}Gd_{0.1}O_{3-d}$ catalysts (Me = Pt, Rh, Ru). The reaction characteristics of the exhaust gas reforming reaction were evaluated by modifying certain reforming conditions, including the temperature, composition of the exhaust gas, hourly space velocity of the gas, and the amount of exhaust gas used. Using lean-burn exhaust gas, iso-octane and gasoline reforming were first investigated with a traditional liquid fuel reforming catalyst, Pt/CGO (0.5 wt.%). The highest yield of hydrogen was obtained when the exhaust gas ratio was approximately half the fuel ratio in this study. Moreover, the hydrogen yield was maximized at temperatures over 700 °C and a GHSV of approximately 10,000/h. In commercial gasoline tests, catalytic degeneration occurs under 700 °C, and carbon deposition occurs even with small deficiencies of the exhaust gas. Therefore, other precious metal catalysts were investigated for lower-temperature operation. In lower-temperature operation at approximately 600 °C, the Ru/CGO catalyst exhibited better performance in exhaust gas reforming than other noble metal catalysts.

1. Introduction

Continued developments in the automobile industry contribute to humanity. However, the use of fossil fuels, which are primarily consumed by automobiles and are the main sources of CO_2, NO_x, SO_x, and particulate material (PM) emissions, creates major challenges for this industry. Currently, the two main power train systems – the gasoline spark ignition engine (SI) and the diesel compression ignition engine (CI) – face significant problems because of strictly enforced limitations on fuel economy and NO_x emissions worldwide. The fuel economy problem has come to the forefront in SI engines because of the limitations of fossil fuels. In contrast, in CI engines, NO_x and PM resulting from the high heat of the CI are considered the main causes of environmental pollution. Due to the aforementioned concerns, hydrogen-consuming vehicle technologies have received attention due to their benefits of improving fuel economy and reducing emissions (Golunski, 2010; Karim, 2003). Hydrogen is used as an additive for combustion in lean-burn combustion engines and increases the rates of reduction of NO_x in selective catalytic reduction using de-NO_x catalysts.

The combustion of hydrogen additives in lean-burn operations has been presented as one of the various technologies for improving fuel efficiency and reducing emissions in internal combustion engines. The addition of hydrogen improves the combustion characteristics by providing high speed of flame propagation and wide flammability limits, especially under lean-burn conditions (Alrazen et al., 2016; D'Andrea et al., 2004; Jamal and Wyszynski, 1994; Ji and Wang, 2009a; Karim, 2003; Ma et al., 2008; Raviteja and Kumar, 2015; Saravanan et al., 2008; Szwaja and Grab-Rogalinski, 2009). Diesel compression ignition engines also

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increase the thermal efficiency of brakes and decrease specific fuel consumption by the combustion of hydrogen additives due to the increased H/C ratio of the fuel and decrease in the duration of combustion. Moreover, the injection of small amounts of hydrogen facilitates the uniform mixing of fuel and air (Alrazen et al., 2016; Saravanan et al., 2008; Szwaja and Grab-Rogalinski, 2009). Combustion of hydrogen additives is also associated with the reduction of various emissions of lean-burn-operating gasoline SI engines (Ji and Wang, 2009b, 2009c, 2010). In the case of diesel CI engines, hydrogen results in the reduction of unburned hydrocarbons (UHCs), CO, CO_2, PM and smoke. Moreover, the combination of hydrogen addition with exhaust gas recirculation system (EGR) can reduce NO_x emissions due to the cooling effect of EGR (Banerjee et al., 2015; Shin et al., 2011).

In vehicles, hydrogen helps improve not only combustion characteristics but also the post-treatment system, particularly selective catalytic reduction (SCR) to reduce NO_x emissions and de-NO_x catalysts (Goula et al., 2016; Houel et al., 2007; Satokawa et al., 2007; Shimizu and Satsuma, 2007; Sitshebo et al., 2009; Zhang et al., 2007). Hydrogen is an effective reductant of NO_x over noble metal catalysts in the absence of oxygen. Even in an oxidizing atmosphere, the reduction of NO_x by hydrogen occurs at low temperatures.

However, hydrogen is difficult to apply in automobile systems because a robust and stable method to extract hydrogen from engine systems is difficult to implement. For this reason, the best alternative method to supply and carry hydrogen in vehicles is an on-board hydrocarbon fuel reforming process. Hydrocarbon fuels (such as gasoline and diesel) provide the most efficient means to carry hydrogen because of its higher volumetric and gravimetric density. Only a small amount of fuel from the main fuel source can supply the hydrogen necessary for this process; thus, hydrogen supplements are feasible without requiring additional equipment for hydrogen storage. However, fuel reforming also requires sustainable supplements of water and air as oxidants for the fuel reforming process. In stationary fuel cell power generation systems, continuous and stable supplementation with oxidizers is possible via the use of an additional water-tank pipe line, air compressor and fuel pipe line (in case of gas fuels, such as natural gas and liquefied petroleum gas). However, in vehicles, the additional water tank and air compressor increase the load. Moreover, increased complexity of the internal system configuration of vehicle systems should be avoided.

In such situations, the exhaust gas of the engine focuses on alternative reforming oxidizers. Engine operation is similar to that of complete combustion reactions of hydrocarbon fuels. Therefore, the engine exhaust gas contains a certain amount of water. Furthermore, in lean-burn-operating engines (or CI engines), the exhaust gas includes a certain amount of oxygen. The water and oxygen components can play the role of an oxidizer in the fuel reforming process. The issue of the amount of water and oxygen required to operate the fuel reforming process has not been resolved.

Previous exhaust gas fuel reforming studies have mainly been conducted using stoichiometric combustion exhaust gases as oxidizers in the reforming process (Ambroise et al., 2009, 2010; Fennell et al., 2015; Gomes et al., 2011; Peucheret et al., 2006; Sen and Avci, 2014a,b; Shudo et al., 2009; Tsolakis and Golunski, 2006; Tsolakis et al., 2003). These gases produce a hydrogen concentration of approximately 11–15% in a dry base.

In this paper, lean-burn-operated exhaust gas, which includes a certain amount of oxygen, was used for exhaust gas reforming. The presence of oxygen in lean-burn-operated exhaust gas leads to autothermal reforming in on-board exhaust gas fuel reforming systems; thus, no additional heating source is required in lean-burn-operated exhaust gas reforming. Therefore, current using autothermal reforming catalysts can be adopt for exhaust gas reforming system. This paper demonstrates the feasibility of CGO based novel metal catalysts, which used current autothermal reforming system. (Han et al., 2016; Lee et al., 2015; Yoon et al., 2011).

2. Experiments

2.1. Exhaust gas compositions

Table 1 shows an example of the composition of exhaust gas emissions of a gasoline SI engine. The data in the table were obtained from experiments with a gasoline spark ignition engine from Hyundai Motors Company. The composition of the exhaust gas varies according to the engine operating conditions. In particular, the condition that most effectively determines the composition of exhaust gases is the air/fuel ratio (AFR) in engines. The composition of the exhaust gas is typically measured by gas chromatography (GC). However, GC is unable to measure the composition of steam in exhaust gases. Therefore, in this work, the amount of water included in the exhaust gas was calculated from the mass balance and the oxygen atom balance of the engine outlet and inlet. After this calculation, it was assumed that the undetected mass in the engine outlet is the mass of water and that the undetected oxygen atoms were completely converted to water. The results of the calculation of the mass of water in exhaust gases broadly corresponded to the mass of fuel used in engine operation, as shown in the last row of Table 1.

2.2. Catalyst

A Gd-doped CeO_2 ($Ce_{0.9}Gd_{0.1}O_{\delta-2}$)-based (CGO-based) platinum catalyst was used for exhaust gas reforming in this study. CGO-based catalysts are known to provide good resistance to carbon deposition, and CeO_2 possesses many oxygen vacancies and a high oxygen ion conductivity, which are important characteristics for hydrocarbon reforming (Krumpelt et al., 2002; Yoon et al., 2009). Platinum (Pt) was initially used as the active material for catalysts. Platinum has been used as a catalyst for heavy hydrocarbon

Table 1
Exhaust gas compositions.

Fuel	AFR	Exhaust gas				
amount kg/h		ExT °C	NOx ppm	CO %	CO_2 %	O_2 %
2.487	19.0	469	976	0.1	10.7	5.34
3.721	20.1	518	855	0.1	10.2	6.08
1.665	18.8	388	918	0.1	11.0	5.19
4.335	21.6	521	875	0.1	9.6	7.27
5.478	24.4	516	860	0.1	8.4	8.73
11.157	20.0	678	746	0.1	10.4	5.89

AFR: Air Fuel ratio.
ExT: Exhaust Temperature.