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CARBON DIOXIDE ZERO-EMISSION HYDROGEN CARRIER SYSTEM FOR FUEL CELL VEHICLE

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Fuel cell (FC) offers the possibility of expanding new vehicle market. One of the key technologies that will make the widespread use of FCs possible is efficient and safety hydrogen supply system. The possibility of a hydrogen carrier system for FC vehicles, which utilized chemical reactants and capable to supply hydrogen safety with no carbon dioxide emission, was discussed in this study. The system uses a portable thermally regenerative fuel reformer of carbon dioxide fixation type. The reactivity of metal oxide to carbon dioxide was used for the carbon dioxide fixation, hydrogen purification and also for heat source of fuel reforming. In the experimental study, calcium oxide was used as the first candidate for carbon dioxide fixation and methane was chosen as a candidate reactant for steam reforming. Fuel reforming, carbon dioxide fixation and pure-hydrogen production were examined by a laboratory scale packed-bed reactor. High-purity hydrogen production under mild operation conditions was demonstrated. The fixed carbon dioxide can be decarbonated thermally by consuming high-temperature heat source. Nuclear power, unstable energy sources such as renewable energy, surplus industrial process heat and so forth are applicable on the system. The contribution of nuclear power and other thermal energy sources on the zero-emission hydrogen career system was evaluated based on the experimental results. The reactor size was more compact than conventional hydrogen career systems. Because the reforming system supplies hydrogen safety on-board to a vehicle FC and the reformer is thermally regenerative, the proposed system was expected to develop new hydrogen market for FC vehicle.

Keywords: zero emission; fuel cell; fuel reforming; hydrogen energy; calcium oxide.

INTRODUCTION

Fuel cells offer the possibility of expanding the electricity utilization market. Vehicles are seen as particularly good candidates for fuel cell application, because fuel cells are more compact, quieter and emit cleaner exhaust gas than conventional internal combustion engines.

One of the key technologies that will make the widespread use of fuel cells possible is a hydrogen supply system. The uses of liquefied or compressed hydrogen are candidates for this technology. However, the storage and transportation of either of these forms of hydrogen require large amounts of energy as well as stringent safety precautions. These drawbacks make steam reforming of common fuels, such as methane, propane, methanol and kerosene, more practical solution for storing and supplying hydrogen. Steam reforming can occur at the site of the fuel cell.

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The use of any of these chemical reactants as a hydrogen storage medium presents the possibility of a safe hydrogen carrier and supply system. On the other hand, the reforming requires additional apparatuses for hydrogen production, including at least three: a steam reforming reactor, a burner for reforming heat supply and a carbon monoxide converter.

In vehicles, it is especially important for a fuel cell reformer to be compact and lightweight. A concept of a thermally regenerative steam fuel reformer for a vehicle had been proposed (Kato *et al.*, 2003). This paper showed that a fuel cell system using the reformer can achieve zero carbon dioxide emission driving by chemical fixation of carbon dioxide and utilize of thermal output form a high-temperature heat source, and estimated experimentally a possibility of the regenerative reformer system.

CONCEPT OF THERMALLY REGENERATIVE REFORMER FOR A VEHICLE

Regenerative Reformer

In this study, methane (CH_4) was chosen at first as a candidate reactant for steam reforming, because it is the most popular natural fuel resource and has a simple hydrocarbon fuel structure. The following regenerative reformer methodology is applicable also to kerosene and propane, both of which have reforming temperatures in the range of 700–900°C, similar to that of methane. The CH_4 steam reforming process consists of the following two gas phase reactions with various catalysts.

Methane steam reforming:

$$CH_4(g) + H_2O(g) \longleftrightarrow 3H_2(g) + CO(g), \quad \Delta H_1^\circ = +205.6\,\text{kJ mol}^{-1} \tag{1}$$

Carbon monoxide (CO) shift reaction:

$$CO(g) + H_2O(g) \longleftrightarrow H_2(g) + CO_2(g), \quad \Delta H_2^\circ = -41.1\,\text{kJ mol}^{-1} \tag{2}$$

This study attempts to use calcium oxide (CaO) carbonation to remove carbon dioxide (CO_2) from the reformed gas and fix it.

Carbonation of calcium oxide:

$$CaO(s) + CO_2(g) \longleftrightarrow CaCO_3(s), \quad \Delta H_3^\circ = -178.3\,\text{kJ mol}^{-1} \tag{3}$$

This study aims to cause equation (1), (2) and (3) reactions in the same reactor at once. These reactions, taken as a whole, are defined as regenerative reforming.

Regenerative reforming:

$$CaO(s) + CH_4(g) + 2H_2O(g) \longleftrightarrow 4H_2(g) + CaCO_3(s), \quad \Delta H_4^\circ = -13.3\,\text{kJ mol}^{-1} \tag{4}$$

Conventional steam reforming is depicted in Figure 1(a). CH_4 and water (H_2O) react by equation (1) in a catalytic reformer, and the generated CO is shifted by equation (2) into CO_2 and H_2 in a catalytic converter. The endothermic reforming process needs a heat supply of ΔH_1°. The proposed process is shown in Figure 1(b). This process consists of a reforming process [Figure 1(b-1)] while the vehicle is driving and a regenerating process [Figure 1(b-2)] for calcium oxide regeneration and carbon dioxide recovery while the vehicle is turned off. CaO and a reforming catalyst mixture are packed in a regenerative reformer. Reactants are reformed by equation (1), and generated CO_2 is removed from the gas phase by the CaO carbonation of equation (3). The CO shift reaction of equation (2) is enhanced under the non-equilibrium condition realized by the CO_2 removal. Purified H_2 is generated from the reactor finally.

The whole reaction of equation (4) is exothermic, hence the reaction needs no heat supply and can proceed spontaneously. A zero CO_2 emission drive is possible due to CO_2 fixation resulting from the carbonation.

In the regenerating process, CaO is regenerated from $CaCO_3$ in the reactor using high-temperature heat from surplus process heat or from surplus night electricity. Regenerated CO_2 is managed according to a CO_2 recovery process. The proposed regenerative reformer is intended to be contained in a removable package for use in a fuel cell vehicle. The package is loaded into and recovered from a vehicle at a regeneration station that supplies new packages and regenerates used ones.

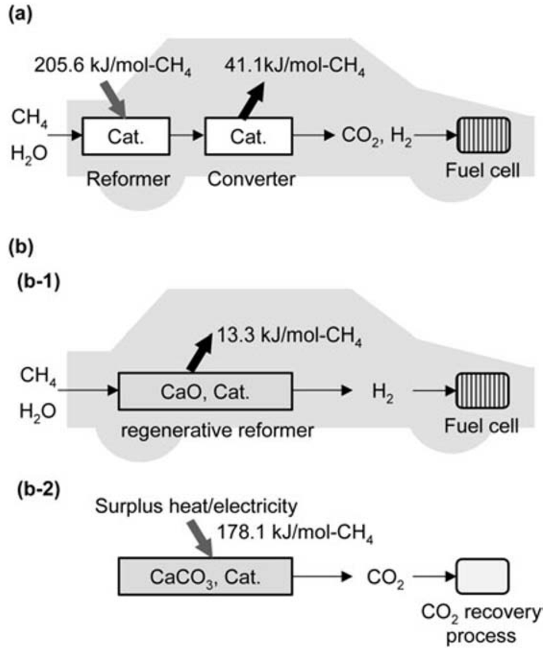

Figure 1. Concept of a carbon dioxide zero-emission vehicle using a thermally regenerative reformer; (a) conventional reforming, (b) proposed thermally regenerative reforming, (b-1) reforming mode, (b-2) regenerating and carbon dioxide recovering mode.

CO_2 Zero-Emission Fuel Cell Vehicle System

The concept of a CO_2 zero-emission fuel cell system using the regenerative reforming process depicted in Figure 1(b) is proposed in Figure 2. The CO_2 zero-emission system consists of fuel cell cars using packages of the regenerative reformer, a decentralized package regeneration station, and power plant systems for thermal energy supply. The regeneration station plays central role in the system. The packages are loaded in fuel cell vehicles. The vehicles are driven by hydrogen fuel produced from the packages. The packages after reforming are collected to the regeneration station. The packages are regenerated, that is, decarbonated thermally using joule heat produced by electricity from renewable energy system or nuclear power plant, and heat output from high-temperature industrial process. Regenerated packages are reused repetitively in the cars. Generated CO_2 is recovered in a storage vessel, and is treated at a hydrogenation process for methane regeneration or CO_2 fixation processes. A comprehensive CO_2 zero-emission system is formed using those CO_2 treatment processes. The system was expected to contribute on load leveling of nuclear power plant operation by utilizing surplus electricity or heat of the plants as heat source for the CaO and CH_4 thermal regeneration processes. Because the system is acceptable unstable thermal energy input, the system would realize stable load operation of renewable energy system and power plants. Utilize of nighttime electricity in the system would be advantageous for economical power plant operation.