Compact design of oxidative steam reforming of methanol assisted by blending hydrogen peroxide

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ABSTRACT

Oxidative steam reforming of methanol (OSRM) mixed with hydrogen peroxide was investigated as a compact hydrogen source for mobile fuel cell systems and a catalytic reactor was designed to validate the concept. The catalytic decomposition of hydrogen peroxide released the heat, oxygen and water vapor, all of which served OSRM. As the heat was generated internally by the decomposition of the liquid hydrogen peroxide, the reactor ran without external supply of heat and vaporizers for liquid reactants. The platinum/γ-Al_2O_3 catalyst was used, because Pt was active in the decomposition of hydrogen peroxide as well as methanol reforming. The optimal operation condition was determined from the parametric study of H_2O_2/CH_3OH mixture ratios of the liquid reactant supplied to the reforming reactor. The concentration of hydrogen peroxide at 70 wt% was selected to avoid detonation of its mixture with organic substance such as alcohol. The reforming performance was best among the test conditions when the mixture ratio of 70 wt% H_2O_2/CH_3OH was 3.036. The investigation demonstrated the proposed concept of methanol reforming is effective alternative to the existing OSRM without auxiliary reactors for treatment of reactants and external heat supply.

Introduction

The proton exchange membrane fuel cell (PEMFC) is an attractive alternative power source for mobile systems [1,2]. However, a compact supply of gaseous hydrogen is required for its operation. A number of hydrogen supply methods have been researched for decades. None of them has yet satisfied requirements of a portable PEM fuel cell. Pressurized hydrogen and liquefied hydrogen require heavy and expensive storage tank. On-board production of hydrogen by reforming a liquid fuel is a viable option but requires auxiliary devices such as evaporators and an external heat supply system [3–6].

In this study, the decomposition of hydrogen peroxide was used for compact design of methanol reforming. Among the liquid fuel candidates, methanol has many advantages over other fuels; methanol is safe to handle and inexpensive [3,6–9]. In addition, methanol can be reformed at a relatively low temperature with a lower risk of coke formation due to its high hydrogen to carbon ratio, low boiling temperature, and no C–C bonding [1,2,6,10–12]. Hydrogen can be produced by partial oxidation of methanol (POM), steam reforming of
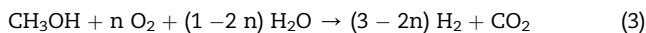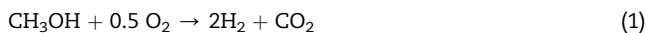
methanol (SRM), and oxidative steam reforming of methanol (OSRM).

$$CH_3OH + 0.5 O_2 \rightarrow 2H_2 + CO_2 \quad (1)$$

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (2)$$

$$CH_3OH + n O_2 + (1 - 2n) H_2O \rightarrow (3 - 2n) H_2 + CO_2 \quad (3)$$

Equation (1) represents POM, which is an exothermic reaction with quick start-up. The theoretical concentration of hydrogen in the product gas of POM is low at 67% and the CO concentration is higher than that of the SRM [13–16]. The SRM, represented by Eq. (2), generates product gas with a high theoretical hydrogen concentration of 75% and a CO concentration of less than 1% [4,14,17–24]. However, the SRM is an endothermic reaction and an external supply of heat is necessary to sustain the reaction. Start-up of the SRM reaction is slower than that of the POM. OSRM, represented by Eq. (3), is a combined reaction of POM and SRM with quick start-up. In an OSRM reactor, heat generated by the exothermic POM reaction sustains the endothermic SRM. The coefficient, n, in Eq. (3) is a key parameter that determines the heat generation and concentration of hydrogen in the product gas [25–28].

All the ingredients of the reforming reaction can be derived from the decomposition of hydrogen peroxide as in Eq. (4), which generates water vapor, gaseous oxygen, and heat for the conventional oxidative steam reforming of methanol in Eq. (3).

$$H_2O_2 + m H_2O \rightarrow (m + 1) H_2O + 0.5 O_2 \quad (4)$$
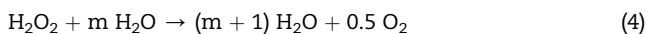
Eq. (4) represents the catalytic decomposition of hydrogen peroxide–water mixture, where m is the number of moles of H_2O per unit mole of H_2O_2. The amount of hydrogen peroxide–water mixture, **x**, that is required for oxidative steam reforming of methanol-hydrogen peroxide (OSRMH), must provide sufficient O_2 and H_2O as shown in the right hand side of the following equation;

$$\mathbf{x} H_2O_2 + \mathbf{x}m H_2O \rightarrow \mathbf{x}(m + 1) H_2O + 0.5\mathbf{x} O_2 \quad (5)$$
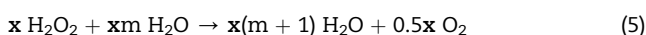
The product side of reaction in Eq. (5) supply O_2 and H_2O in the reactant side of Eq. (3) that becomes as follows;

$$CH_3OH + \mathbf{x}(m + 1) H_2O + 0.5\mathbf{x} O_2 \rightarrow (3 - 2n) H_2 + CO_2 \quad (6)$$
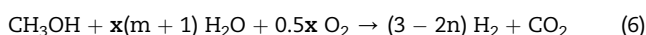
Balancing the numbers of O and H atoms in Eq. (6), **x** and n are determined as follows;

$$\mathbf{x} = 1/(m + 2) \text{ and } n = 0.5 - (m + 1)/(2m + 4)$$

Substitution of **x** and n into Eq. (6) yields following oxidative steam reforming of methanol-hydrogen peroxide (OSRMH).

$$CH_3OH + (m + 1)/(m + 2) H_2O + 0.5/(m + 2) O_2 \rightarrow \{2 + (m + 1)/(m + 2)\} H_2 + CO_2 \quad (7)$$
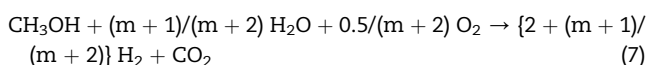
From inspection of the balance equations, following theoretical molar mixture ratios can be derived;

$$H_2O/CH_3OH = (m + 1)/(m + 2) \quad (8a)$$

$$O_2/CH_3OH = 0.5/(m + 2) \quad (8b)$$

Both of the molar ratios depend on the concentration of hydrogen peroxide only and represent the theoretical lower limit of the hydrogen peroxide supply in the reactant. It is shown in Section 2.2. Due to the heat loss to the surrounding and finite reactor volume, much higher supply of hydrogen peroxide must be supplied for efficient OSRM reaction. The optimum supply rate was determined by experimental parametric study in this research.

The use of hydrogen peroxide in the methanol reforming was investigated by Kawamura et al. [29] who used Cu–Zn for methanol reforming in a temperature-controlled furnace along with external device for fuel evaporation. The effect of the decomposition heat of hydrogen peroxide was not clearly demonstrated in the study because the temperature was maintained in an electrical oven and Cu–Zn was not effective catalyst for decomposition of hydrogen peroxide. Therefore, the potential advantage of using hydrogen peroxide in methanol reforming was not fully exploited in the study.

In the present study, a liquid mixture of H_2O_2 and CH_3OH was directly fed into a single reactor not heated by an external heat source. The platinum was selected as the catalyst because it was effective in decomposition of hydrogen peroxide as well as in methanol reforming [30–35]. As the heat generation and reforming process simultaneously occurred in a single reactor with liquid phase reactant supplies, the reactor does not require auxiliary devices for reactant evaporation and heat supply.

Theoretical reaction mechanism of oxidative steam reforming of $CH_3OH–H_2O_2$

The concentration of hydrogen peroxide and the mixture ratio of hydrogen peroxide to methanol, H_2O_2/CH_3OH are two important parameters for the oxidative steam reforming of methanol-hydrogen peroxide to be considered in the present study. Hydrogen peroxide is available as a mixture with water. Depending on the concentration and quantity of hydrogen peroxide, the amounts of water vapor, oxygen, and heat generated by its decomposition vary.

Selection of hydrogen peroxide concentration

Fig. 1 shows the adiabatic decomposition temperature of hydrogen peroxide as a function of its concentration calculated by procedures of Gordon and McBride [36]. When the concentration of hydrogen peroxide is lower than 63 wt%, the heat of decomposition is not sufficient to evaporate all the liquid water in the mixture. As the concentration increases, the decomposition temperature increases in proportion. Liquid hydrogen peroxide containing organic substances is