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Thermodynamic optimization for coupled steam and oxidative reforming for hydrogen production

S.-J. Song*, J.-K. Kim, J.-H. Moon and J.-S. Lee

School of Materials Science and Engineering Chonnam National University 300 Yongbong-dong, Buk-gu, Gwangju, 500-757, S. Kor

Thermodynamic studies were carried out to show that the heat of the autothermal reaction obtained by coupling the endothermic steam reforming process with the exothermic partial oxidation of methane is sufficient to bring the membrane to the temperature required for hydrogen permeation. From the thermodynamic calculation, the autothermal reaction can be optimized for maximizing the hydrogen production by decreasing the O/M (oxygen to methane) ratio and increasing the S/M (steam to methane) ratio.

Key words: autothermal reaction, hydrogen separation.

Introduction

Hydrogen is considered an ideal choice of next generation fuel due to its environmental benefits [1] even though there are great technological difficulties involved in its production, storage, and transportation. One of the key technologies for the "hydrogen economy" is a pure hydrogen production method from ample energy resources with a minimum energy expense. Among the various hydrogen production technologies, the steam reforming of natural gas is one of the conventional methods used for the large-scale production of hydrogen [2, 3]. However, both the strong endothermicity of the overall process and the development of long term, stable and coke resistant catalysts are have been cited as significant technological challenges which remain to be overcome[4]. In the last few years, mixed protonic-electronic conducting ceramics [5-7] have received increasing attention as potential membranes [8-10] for separating hydrogen from syngas or pressurized steam [11] without an external current supply. However, their chemical stability and mechanical integrity at elevated temperature and pressure have been brought into questions [12].

Recently, the autothermal process has been suggested as a means of achieving a thermal energy balance [13]. By coupling the endothermic steam reforming process with the exothermic partial oxidation of methane, highly efficient reaction may take place in one reactor incorporating both oxygen and hydrogen permeable membranes. In addition, the heat energy required to heat up the membrane reactor to the operational temperature can be provided by the simple oxidation of methane. The more salient features of coupled autothermal reactions are a reduced rate of carbon deposition and a more favorable thermal equilibrium that can be achieved as a function of the oxygen feed [14]. Oxygen is fed through oxygen separation membranes to the reactor, which drives the oxidation of methane and liberates the heat required for the endothermic steam reforming reaction. Then, hydrogen may be separated through hydrogen separation membranes, resulting in the thermodynamic equilibrium being pushed toward higher hydrogen yields [15]. Furthermore, a water-gas-shift-reaction reactor [16] may be applied to reduce the amount of carbon monoxide produced and to maximize the hydrogen production in the gas stream after the membrane reactor.

The purpose of this study is to develop efficient hydrogen production technology by simply flowing a hydrogen-rich gas stream through a separation membrane reactor. In this work, the autothermal temperature obtained by coupling the endothermic steam reforming process with the exothermic partial oxidation of methane was calculated as a function of the heat transfer efficiency. The thermodynamics for the autothermal reaction is studied as a function of O/M (oxygen to methane) and S/ M (steam to methane) ratios in the feed gas.

Simulation results and discussion

The autothermal reaction is a combination of steam reforming (Eq. 1) with the partial oxidation of methane (Eq. 2) at such a ratio that the overall reaction may be thermally neutral or exothermic. We need to confirm whether Eq. 3 is a self-sustaining autothermal reaction over a wide range of coupling ratios.

$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{1}$$

$$CH_4 + O_2 = CO_2 + 2H_2 \tag{2}$$

$$CH_4 + yO_2 + 2xH_2O = CO_2 + 2(2x+y)H_2$$
, where $x+y=1$. (3)

^{*}Corresponding author:

Tel : +82-62-530-1706

Fax: +82-62-530-1699

E-mail: song@chonnam.ac.kr

As can be seen in Fig. 1, the endothermic reaction may be provided with the energy required to sustain it at most of the coupling ratios of steam reforming to the partial oxidation of methane at temperatures above 700 oC. In this way, the thermal requirement for the creation of the autothermal reaction may be satisfied. Another important question is whether the heat of reaction is sufficient to bring the membranes to the temperature required for efficient hydrogen permeation. Therefore, we calculate the autothermal temperature that can be obtained by coupling the endothermic steam reforming process with the exothermic partial oxidation.

For the autothermal temperature, the molar ratio of the oxygen feed to water vapor is a key performance parameter.

$$\Delta H_{298}^{\circ} = \eta \cdot \left(\int_{298}^{T} \Delta C_P \ dT + \Delta H_{H_2O}^{l \to g} \right)$$
(4)

where η is the heat transfer efficincy.

Figure 2 shows the autothermal temperature calculated as a function of the heat transfer efficiency with various ratios of partial oxidation to the steam reforming reaction. When the oxygen content is higher than that of water vapor, the autothermal temperature exceeds 4000 °C, which is not only unnecessarily high, but also undesirable. However, as long as the ratio of oxygen to water vapor remains below 0.21, the autothermal temperature comes down to below 2000 °C, showing that it is controllable. It should be pointed out, however, that as hydrogen is separated with a hydrogen permeable membrane, this extraction may enhance the endothermic steam reforming reaction, resulting in decrease of the autothermal temperature. Therefore, the addition of oxygen through oxygen permeable membranes or a direct external supply provides the heat required for the endothermic reaction and, in this way, optimum autothermal conditions can be maintained.

Thermodynamic calculations based on the given chemical

reaction equilibrium, Eq. 3, assumes that all the reactants are converted quantitatively into the product. However, the equilibrium composition may not be the same as the theoretical one, due to the complexity of the system. The multi-component equilibrium composition in the systems was calculated by using the Gibbs energy minimization method. Figure 3a shows the calculated equilibrium composition of the system Eq. 3 for x =0.5, y = 0.5. The composition profile shows a maximum hydrogen yield near 700 °C with the starting gas mixture and the hydrogen production rate remains constant. The profile of methane conversion in Fig. 3b also shows a complete conversion around 700 °C. According to the calculated equilibrium composition shown in Fig. 3, the hydrogen yield is mainly determined by the formation of water vapor and methane conversion. The conversion of methane is represented by the formation of CO and CO₂ if there is no carbon deposition. The methane conversion was essentially complete for temperatures above 700°C. However, the equilibrium composition above 700°C still contains a considerable amount of CO and water vapor. Thus, for efficient hydrogen production and minimum CO production, the use of the water gas shift reaction after the membrane reactor is suggested.

$$CO+H_2O=CO_2+H_2\tag{5}$$

For the water-gas-shift-reaction, the molar ratio of CO and CO2 products in the autothermal reaction reactor is an important factor. The CO/CO₂ ratio increases with increasing temperature. Therefore, the operational membrane temperature may be optimized at around 900 °C with both a maximum CO/CO₂ ratio and high methane conversion.

The effect of the O/M ratio on the conversion of methane and the hydrogen yield is shown in Fig. 4. As the O/M ratio increases in the feed gas, more water vapor and CO_2 are produced, whereas hydrogen and CO are the main products at lower O/M ratios. These



Fig. 1. Variation of Gibbs free energy with feeding ratio.



Fig. 2. Autothermal temperature as a function of heat transfer efficiency.



Fig. 3. (a) Equilibrium composition, (b) relative composition as a function of temperature.

two distinct reaction regimes were reported by the CHEMKIN simulation work [17] during the partial oxidation of methane. According to Zhu et. al., one regime is a "rapid" conversion zone where water vapor and CO_2 are the main reaction products. The other regime is a "slow" conversion zone where steam and CO_2 reforming as well as the water gas shift reaction takes places with hydrogen and CO being the main products. Therefore, the O/M ratio should remain below 0.75 at temperatures above 700 °C for the purpose of maximizing the production of hydrogen and CO in the autothermal reactor.

The effect of the S/M ratio on the equilibrium composition is also studied in Fig. 5. The steam to methane ratio in this study corresponds to the amount of water being added to the reactor relative to the amount of methane in the feed gas on a molar basis with 0.5 mol of oxygen. The equilibrium composition profile shows an increase in the amount of hydrogen and a decrease in amount of CO produced with increasing S/M ratio. This region also belongs to the slow conversion zone where the water-gas-shift reaction takes places. Therefore, increasing the S/M ratio at a given O/M ratio generates more hydrogen and less CO.



Fig. 4. Effect of methane to oxygen ratio on hydrogen production.



Fig. 5. Effect of methane to steam ratio on hydrogen production.

Conclusions

Thermodynamic studies were carried out to show that the heat of the autothermal reaction obtained by coupling the endothermic steam reforming process with the exothermic partial oxidation of methane is sufficient to bring the membrane to the temperature required for hydrogen permeation. From the thermodynamic calculation, it was found that the autothermal reaction can be optimized for the purpose of maximizing the hydrogen production by decreasing the O/M ratio and increasing the S/M ratio.

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