

Low-Temperature Reforming for Fuel Cells

연료전지를 위한 저온 개질

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1. Introduction

Fuel cells are energy conversion devices that produce electricity directly from a gaseous fuel by electrochemical combination of the fuel with an oxidant [1]. Compared with internal combustion engine, wherein its maximum efficiency is restricted by Carnot cycle principle, fuel cell systems work more efficiently (theoretical efficiency could be 100%) and produce less emission (if hydrogen is used as fuel, the only emission is water) [2]. So, fuel cells being environmentally benign and highly efficient represent a promising technology for converting chemical energy of a fuel directly into electricity without a thermal cycle. Since the first significant application of fuel cell technology in the Gemini space program of NASA in 1960s, fuel cell technology now has considerably matured: various types of fuel cells are available for specific applications with a wide range of electrical power output, ranging from less than 1 kW up to several MW [3]. From 1980s, especially in the turn of the new century, the energy crisis and the increasing concern about the environmental consequences of fossil fuels used in the production of electricity and for the propulsion of vehicles further stimulated the research and development of these systems. It is recognized that cost is still a major issue for the wide application of fuel cells. Exactly, this is one of the major driving forces for further research and development.

The main fuel for fuel cells is hydrogen. The missing hydrogen infrastructure and the unsolved hydrogen storage problem have initiated the development of compact fuel reformers that are able to produce a hydrogen rich gas from fuels such as hydrocarbons. Methane (the main constituent of natural gas), due to its large abundance and high H/C ratio, is an ideal source of hydrogen. The on-board production of hydrogen for fuel cells has been intensively investigated in recent years [4,5]. To date, hydrogen production from methane can be achieved through steam reforming (SRM), partial oxidation of methane (POM) both catalytically and non-catalytically, carbon dioxide reforming (CDR), and the combination of SRM and POM, i.e. oxy-steam reforming (OSRM) over nickel and/or precious metal catalysts [6-10]. But, methane is a refractory molecule with a high C-H bond dissociation energy of 104 kcal/mol [11], high temperature (typically above 800 °C) is required to achieve a high conversion of CH₄ during SRM, POM, CDR and OSRM processes. As a result, special alloy materials are required for manufacturing the reactor increasing thereby a high material cost. To overcome these

disadvantages such as high initial investment and high-energy consumption associated with the high operating temperature, the present investigation aims at studying the reforming of methane at low temperatures based on a catalyst with high activity and stability.

2. Experimental

2.1. Catalyst

The support material used in this study was prepared as follows. The solution of mixed Ce-acetate/Zr-nitrate ($\text{CeO}_2/\text{ZrO}_2 = 0.25$ w/w) was impregnated on $\gamma\text{-Al}_2\text{O}_3$ at room temperature for 12 h. The precoated sample was calcined at 900 °C for 6 h with a heating rate of 1 °C/min. During the heat treatment, $\gamma\text{-Al}_2\text{O}_3$ was transferred to $\theta\text{-Al}_2\text{O}_3$. Nickel was loaded by impregnating appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on the support for 24 h and followed by drying at 100 °C. After drying, the sample was calcined in air at 550 °C for 6 h. The nickel loading was 12 wt.%.

2.2. Reaction procedure

The experiments of SRM, POM and OSRM were carried out at atmospheric pressure in a fixed-bed reactor system. The reactor (Incolloy 800H) with an inner diameter of 18 mm was heated in an electric furnace. The bed temperature was monitored by a K-type thermocouple placed in the center of the catalyst bed with a thermowell. The feed was a mixture of CH_4 , steam and/or O_2 . Gaseous reactants (CH_4 and/or O_2) were controlled and monitored by mass flow controller. Water was added to the feed by using a HPLC pump (F6100, FUTECS) and a specially designed evaporator. Before reaction, two grams of catalyst with a particle size of 16-20 mesh were loaded and reduced at 700 °C for 3 h with 5% H_2 in N_2 . The catalytic reactions were carried out at different temperatures, gas hourly space velocities (GHSV) and molar ratio of reactants in the feed. A cold trap at the outlet of the reactor was used to condense any water from the product gas stream. The product gases were analyzed by an on-line GC equipped with a TC detector, using a Carbosphere packed column (Alltech) and Ar as a carrier gas.

3. Results and discussion

3.1. Hydrogen production at low temperatures

Because of the increased demand for hydrogen, both for petroleum refining processes and for the petrochemical use in the production of methanol, ammonia, and hydrocarbon synthesis through syngas route, several processes for the production of hydrogen or syngas from CH_4 have been proposed as mentioned above. Among them, SRM yields the highest percentage of hydrogen. For an example, a POM reformer would produce only about 75% of the hydrogen (after shifting) that was produced by a SRM reformer [5]. But, SRM is a highly energy intensive process because of the highly endothermic property of the reaction. So, high

temperature is favorable for SRM.

To study the properties of SRM at low temperatures, thermodynamic equilibrium was calculated by using HSC Chemistry (Ver. 3.0, Outokumpu Research Oy, Finland) under different steam to CH₄ (S/C) ratios and pressures. The effects of S/C ratio and temperature on CH₄ conversion, H₂ content in dry tail gas and H₂ yield are illustrated in Fig. 1. CH₄ conversion increased almost linearly with increasing temperature until 97.1% at 700 °C for S/C=3.0. Moreover, it was clearly shown that both CH₄ conversion and H₂ yield are favorable at high S/C ratio under the temperatures investigated. It is worthy to note that both H₂ content in dry tail gas and H₂ yield increase almost linearly with increasing temperature from 400 °C to 600 °C for S/C=3.0. After that, when temperature is further increased to 700 °C, H₂ content in dry tail gas and H₂ yield increase slowly, which is mainly caused by the inhibition of water gas shift (WGS) reaction at higher temperatures.

From the above thermodynamic results, there is still a certain amount of CH₄ unconverted when SRM is operated at low temperatures. To improve the total efficiency of SRM at low temperatures, a process of hydrogen production was proposed based on the burning of the unconverted CH₄ for steam generation, reactant preheat and SRM reformer heating. Under the following conditions, 1) Heat is consumed for generating steam, preheating the feed to the desired temperature and providing the reaction heat of SRM (49.3 kcal/mol irrespective of reaction temperature); 2) Heat is produced by burning the unconverted CH₄ under the equilibrium conditions; 3) The heat loss is neglected and 100% heat efficiency is expected; 4) The feed composition fixed at a S/C ratio of 3, the initial temperature taken as 25 °C and atmospheric pressure were used for calculation, it was calculated that heat balance could be achieved at 548 °C.

On the other hand, OSRM, which integrates POM and SRM simultaneously, has many advantages such as low energy requirements due to the opposite contribution of the exothermic methane oxidation and endothermic steam reforming, low specific consumption, high gas hour space velocity (at least one order of magnitude relative to traditional SRM) and variable H₂/CO ratio regulated by varying the feed composition. Thermodynamic analysis indicates that the optimal operating regime for natural gas is molar air to fuel ratio of 3.5 and water to fuel ratio of 2.5-4.0 [4]. The products temperature under the assumption of adiabatic reaction corresponding to the above conditions is 547 °C to 598 °C. This motivated us to study the properties of OSRM at low temperatures over Ni/Ce-ZrO₂/θ-Al₂O₃.

From the above results and analysis, it is expected that SRM and OSRM are feasible thermodynamically at low temperatures.

3.2. SRM at low temperatures

Fig. 2 shows the reaction results of SRM over Ni/Ce-ZrO₂/θ-Al₂O₃ at different temperatures. Comparing the experimental and thermodynamic values shown in Fig. 2, it is clear that

thermodynamic equilibrium was achieved under all the temperatures investigated, suggesting that the catalyst is very active for SRM at low temperatures. At the same time, experimental CH₄ conversion increased almost linearly with increasing reaction temperature from 400 °C to 650 °C, which confirms that higher temperature is favorable for SRM. Moreover, the observed higher H₂/CO ratio (>6.0) indicates that WGS reaction occurred to a great appreciable extent simultaneously with SRM. At the same time, the increase in CO selectivity and the decrease in H₂/CO ratio with increasing reaction temperature were consistent with the fact that WGS reaction was thermodynamically unfavorable at higher temperatures. It is worthy to note that H₂ content increased sharply with increasing temperature from 400 °C to 550 °C. After that, it increased very slowly and reached 74.5% at 650 °C. This was explained in terms of the contribution of SRM reaction and WGS reaction to the hydrogen content in dry tail gas. Increasing reaction temperature, more hydrogen was produced as a result of the increase of CH₄ conversion. But, WGS reaction was inhibited at higher temperature resulting in less hydrogen production. The above observation was a result of the balance of the two reactions.

Moreover, Ni/Ce-ZrO₂/θ-Al₂O₃ showed near equilibrium CH₄ conversion and H₂ yield for about 200 h without observable deactivation. So, from the above results and discussion, it can be concluded that Ni/Ce-ZrO₂/θ-Al₂O₃ having high activity and stability shows to be an efficient catalyst for SRM at low temperatures.

3.3. OSRM at low temperatures

The influence of O₂/CH₄ ratio in the feed at 650 °C and a fixed space velocity of 7470 ml CH₄/(g_{cat} h) on the conversion, selectivity, H₂/CO ratio during SRM & OSRM has been studied. When the O₂/CH₄ ratio was increased while keeping a constant CH₄ flow rate and H₂O/CH₄ ratio of 1.0, it was observed that CH₄ conversion increased remarkably while O₂ was consumed nearly 100%. Moreover, CO selectivity decreased significantly and hence the H₂/CO ratio increased while the H₂ content in dry tail gas was almost constant. These observations clearly indicate that POM reaction occurred simultaneously with SRM and WGS reactions. The decrease in CO selectivity suggests that the rate of WGS reaction was increased with increasing O₂/CH₄ ratio.

Also, the influence of H₂O addition in the feed on the conversion, selectivity, H₂/CO ratio for POM & OSRM at 650 °C and a fixed space velocity of 7470 ml CH₄/(g_{cat} h) has been tested. When there was no H₂O present in the feed, i.e. POM reaction, CH₄ conversion was only about 56% (CH₄ conversion over the catalyst was about 90% for POM at 750 °C), while O₂ conversion approached 100%. Moreover, the H₂/CO ratio (2.5) was higher than the stoichiometric value of 2.0 for POM. Those observations suggest that complete oxidation of CH₄ occurred to an appreciable extent simultaneously with POM. With the increase of H₂O/CH₄ ratio, both CH₄ conversion and H₂/CO ratio increased sharply suggesting that both SRM and WGS reactions occurred simultaneously besides POM reaction. The significant decrease of CO selectivity with increasing H₂O/CH₄ ratio further confirms the above suggestion.

4. Conclusion

The conclusions drawn from this investigation are as follows.

1. Thermodynamic equilibrium analysis indicates that SRM at low pressure and high S/C ratio can be conducted without significant loss of H₂ yield at a low temperature such as 550 °C.
2. A scheme of the hydrogen production system through SRM for fuel cells at low temperatures was proposed by burning the unconverted CH₄ outside of the reformer to supply the energy for SRM. The calculated heat balance temperature was 548 °C.
3. The Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst showed very high activity which equilibrium CH₄ conversion and product distribution were approached at temperatures from 400 °C to 650 °C. It also showed high stability without observable deactivation for 200 h during SRM at 650 °C.
4. CH₄ conversion increased significantly with increasing O₂/CH₄ or H₂O/CH₄ ratio, and H₂ content in dry tail gas increased with H₂O/CH₄ ratio for OSRM at 650 °C.

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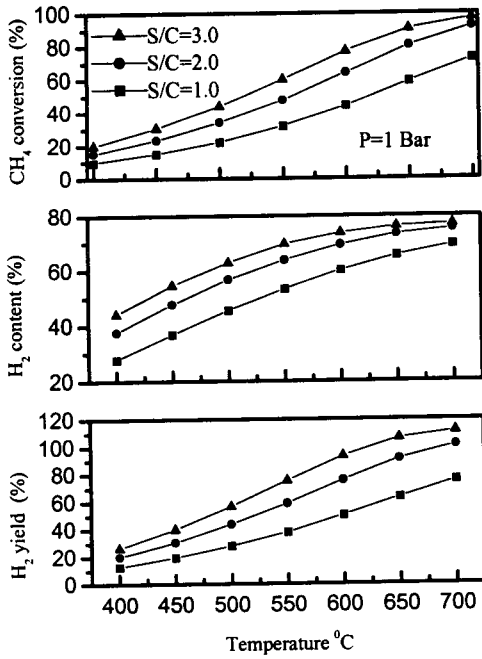


Fig. 1. Effect of temperature and S/C ratio on the equilibrium values of SRM at P=1 atm.

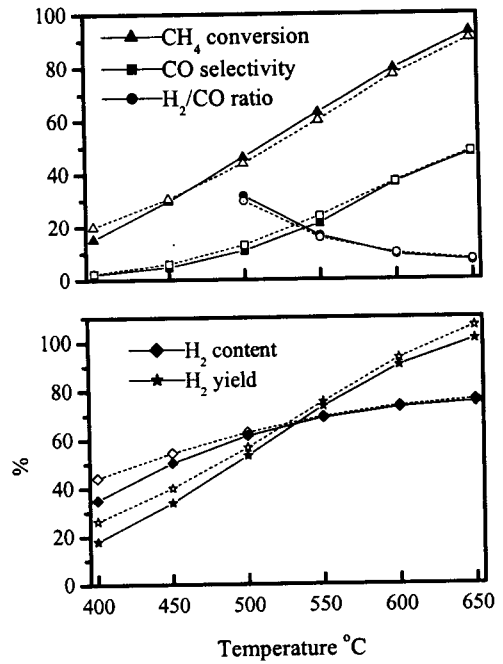


Fig. 2. Effect of temperature on the performance of the catalyst for SRM (hollow symbols: thermodynamic values; solid symbols: experimental values. Operating conditions: P=1 atm, H₂O/CH₄=2.98, GHSV=5010 ml CH₄/(g_{cat} h)).