

Hydrogen production for fuel cells through methane reforming at low temperatures

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Abstract

Hydrogen production for fuel cells through methane (CH_4) reforming at low temperatures has been investigated both thermodynamically and experimentally. From the thermodynamic equilibrium analysis, it is concluded that steam reforming of CH_4 (SRM) at low pressure and a high steam-to- CH_4 ratio can be achieved without significant loss of hydrogen yield at a low temperature such as 550 °C. A scheme for the production of hydrogen for fuel cells at low temperatures by burning the unconverted CH_4 to supply the heat for SRM is proposed and the calculated value of the heat-balanced temperature is 548 °C. SRM with and/or without the presence of oxygen at low temperatures is experimentally investigated over a Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst. The catalyst shows high activity and stability towards SRM at temperatures from 400 to 650 °C. The effects of O₂:CH₄ and H₂O:CH₄ ratios on the conversion of CH₄, the hydrogen yield, the selectivity for carbon monoxide, and the H₂:CO ratio are investigated at 650 °C with a constant CH₄ space velocity. Results indicate that CH₄ conversion increases significantly with increasing O₂:CH₄ or H₂O:CH₄ ratio, and the hydrogen content in dry tail gas increases with the H₂O:CH₄ ratio.

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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 an internal combustion engine, wherein the maximum efficiency is restricted by the Carnot cycle principle, fuel cell systems work more efficiently (theoretical efficiency could be 100%) and produce less emissions (if hydrogen is used as fuel, the only emission is water) [2]. Thus, because fuel cells are environmentally benign and highly efficient, they 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 programme of NASA in 1960s, fuel cell technology has matured considerably: various types of fuel cells are available for specific applications with a wide range of electrical power output that ranges from <1 kW to up to several MW [3]. From the 1980s, especially at the turn of the new century, the energy crisis and the increasing concern

over the environmental consequences of fossil fuels used in the production of electricity and for the propulsion of vehicles have 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. This is one of the major driving forces for further research and development.

The main fuel for fuel cells is hydrogen. The lack of a 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 (CH_4 , 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 [4–7]. To date, hydrogen production from methane can be achieved through steam reforming (SRM), partial oxidation (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 [8–14]. Methane is, however, a refractory molecule with a high C–H bond dissociation energy of 104 kcal/mol [15], and thus, a high temperature (typically above 800 °C)

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is required to achieve a high conversion of CH_4 during SRM, POM, CDR and OSRM processes. As a result, special alloy materials are required for manufacturing the reactor and, thereby, increase the material cost. To overcome these disadvantages of 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 catalyst used in this study was prepared as follows. A solution of mixed Ce-acetate/Zr-nitrate ($\text{CeO}_2/\text{ZrO}_2 = 0.25$ w/w) was impregnated on $\gamma\text{-Al}_2\text{O}_3$ (CONDEA Chemie GmbH) at room temperature for 12 h. The pre-coated sample was calcined at 900°C for 6 h with a heating rate of $1^\circ\text{C}/\text{min}$. 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 an appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on the support for 24 h and then 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 centre of the catalyst bed with a thermowell. The feed was a mixture of CH_4 , steam and/or oxygen. Gaseous reactants (CH_4 and/or oxygen) were controlled and monitored by a mass-flow controller. Water was added to the feed by using a HPLC pump (F6100, FUTECS) and a specially designed evaporator. Before reaction, 2 g of catalyst with a particle size of 16–20 meshes were loaded and reduced at 700°C for 3 h with 5% H_2 in nitrogen. The catalytic reactions were performed at different temperatures, gas hourly space velocities 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 gas chromatograph equipped with a TC detector, using a Carbosphere packed column (Alltech) and argon 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 petrochemical use in

the production of methanol, ammonia, and hydrocarbon synthesis through the syngas route, several processes for the production of hydrogen or syngas from CH_4 have been proposed. Among them, SRM yields the highest percentage of hydrogen of any reforming type. For example, a POM reformer produces only about 75% of the hydrogen (after shifting) that is produced by a SRM reformer [7]. SRM is a very energy-intensive process, however, because of the highly endothermic property of the reaction. Thus, high temperature is favourable for SRM.

To study the properties of SRM at low temperatures, the thermodynamic equilibrium was calculated by using HSC chemistry (Version 3.0, Outokumpu Research Oy, Finland) under different steam-to- CH_4 (S:C) ratios and pressures. The effects of S:C ratio and temperature on CH_4 conversion, H_2 content in dry tail gas and H_2 yield are illustrated in Fig. 1. The conversion of CH_4 increases almost linearly with increasing temperature until 97.1% at 700°C for S:C = 3.0. Moreover, it is clearly seen that both CH_4 conversion and H_2 yield are increased at high S:C ratio under the temperatures investigated. It is worthy to note that both H_2 content in dry tail gas and H_2 yield increase almost linearly with increasing temperature from 400 to 600°C for S:C = 3.0. When temperature is further increased to 700°C , however, the H_2 content in dry tail gas and the H_2 yield increase slowly. This is mainly due to the inhibition of the water-gas shift (WGS) reaction at higher temperatures. As shown in Fig. 2, SRM is greatly suppressed under higher pressures.

From the above results and discussion, it is concluded that at low pressure and high S:C ratio, SRM can be carried out at temperatures as low as 550°C without significant loss of H_2 yield. From the above thermodynamic results, there is still a

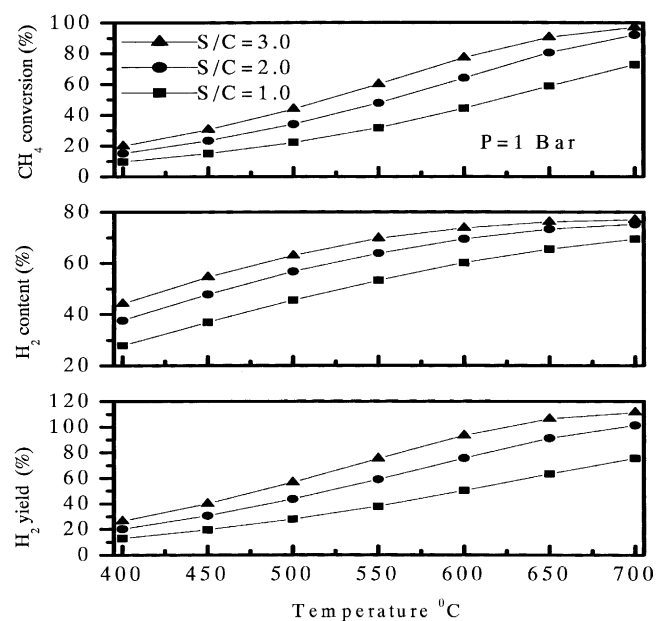


Fig. 1. Effect of temperature and S:C ratio on equilibrium values of SRM at 1 bar.

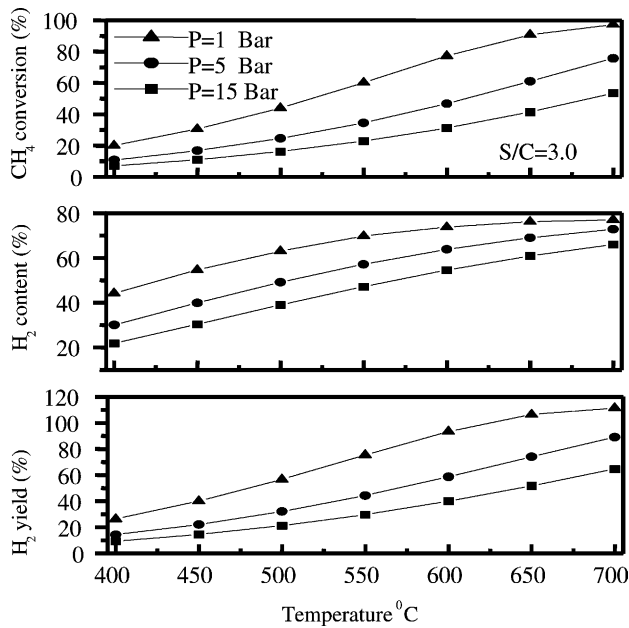


Fig. 2. Effect of temperature and pressure on equilibrium values of SRM at $S/C = 3.0$.

certain amount of CH_4 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 CH_4 for steam generation, reactant preheating and SRM reformer heating, as shown schematically in Fig. 3. It is calculated that heat balance can be achieved at 548°C under the following conditions: (i) 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); (ii) heat is produced by burning the unconverted CH_4 under the equilibrium conditions; (iii) the heat loss is neglected and 100% heat efficiency is expected; (iv) the feed composition fixed at a S/C ratio of 3; (v) the initial temperature is taken as 25°C and atmospheric pressure pertains.

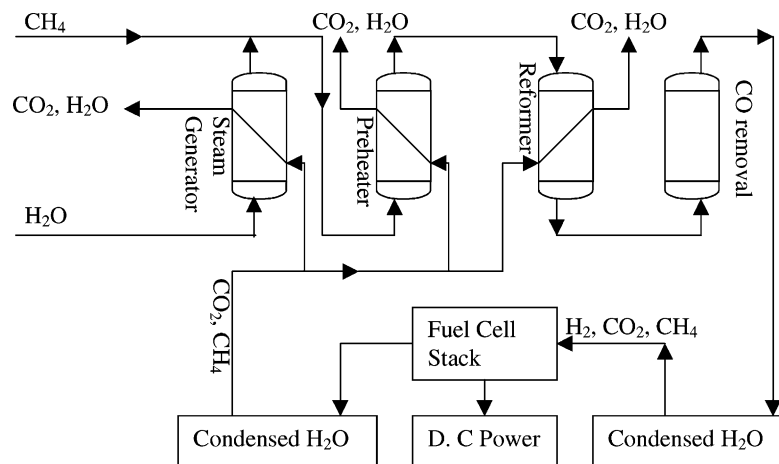


Fig. 3. Schematic diagram of hydrogen production for fuel cells at low temperature.

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); variable $\text{H}_2:\text{CO}$ ratio regulated by varying the feed composition. Thermodynamic analysis indicates that the optimal operating regime for natural gas is a molar air-to-fuel ratio of 3.5 and water-to-fuel ratio of 2.5–4.0 [4]. The temperature of the products with the assumption of an adiabatic reaction corresponding to the above conditions is $547\text{--}598^\circ\text{C}$. This has motivated us to study the properties of OSRM at low temperatures over $\text{Ni/Ce-ZrO}_2/\theta\text{-Al}_2\text{O}_3$.

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

3.2. SRM at low temperatures

The reaction results of SRM over $\text{Ni/Ce-ZrO}_2/\theta\text{-Al}_2\text{O}_3$ at different temperatures are shown in Fig. 4. Comparing the experimental and thermodynamic values, it is clear that thermodynamic equilibrium is achieved under all the temperatures investigated. This suggests that the catalyst is very active for SRM at low temperatures. At the same time, experimental CH_4 conversion increases almost linearly with increasing reaction temperature from 400 to 650°C , which confirms that higher temperature is favourable for SRM. Moreover, the observed higher $\text{H}_2:\text{CO}$ ratio (>6.0) indicates that the WGS reaction occurs to a great appreciable extent simultaneously with SRM. At the same time, the increase in CO selectivity and the decrease in $\text{H}_2:\text{CO}$ ratio with increasing reaction temperature are consistent with the fact that the WGS reaction is thermodynamically unfavourable at higher temperatures. It should be noted that the H_2 content increases sharply with increasing temperature from 400 to 550°C . After this, it increases very slowly and reaches 74.5% at 650°C . This is explained in terms of the contribu-

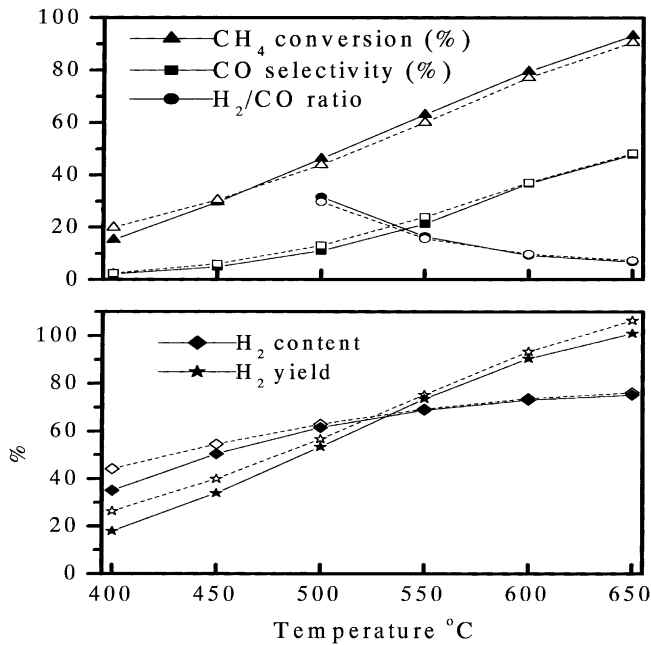


Fig. 4. Effect of temperature on performance of catalyst for SRM. Dash line + hollow symbols = thermodynamic values; solid line + solid symbols = experimental values. Operating conditions: 1 atm; $\text{H}_2\text{O}:\text{CH}_4$, 2.98; GHSV, 5010 ml $\text{CH}_4/(\text{g}_{\text{cat}} \text{h})$.

tion of the SRM reaction and the WGS reaction to the hydrogen content in dry tail gas. On increasing the reaction temperature, more hydrogen is produced as a result of the increase in CH_4 conversion. The WGS reaction is inhibited at higher temperature, however, and results in less hydrogen production. This observation is a result of the balance of the two reactions.

Moreover, $\text{Ni}/\text{Ce}-\text{ZrO}_2/\theta\text{-Al}_2\text{O}_3$ shows near-equilibrium CH_4 conversion and H_2 yield for about 200 h without

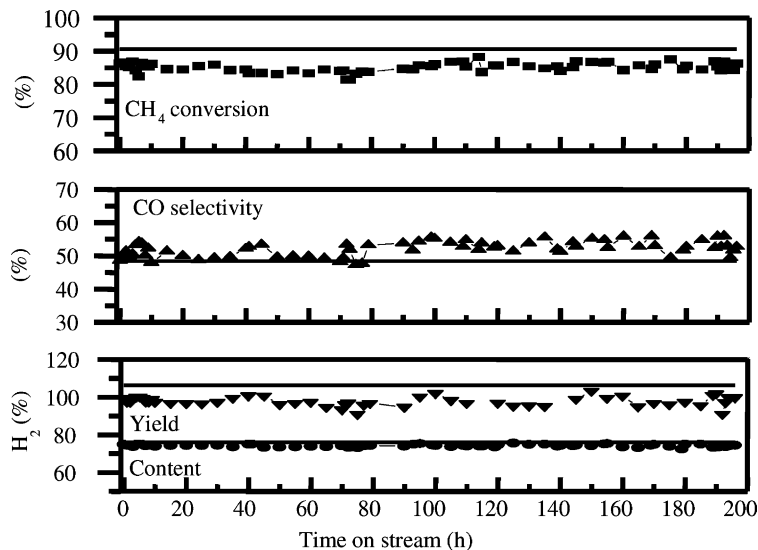


Fig. 5. Stability of catalyst for SRM. Solid line = equilibrium value; symbols = experimental values. Operating conditions: 1 atm; average temperature, 645 °C; S:C, 2.98; GHSV, 1251 ml $\text{CH}_4/(\text{g}_{\text{cat}} \text{h})$.

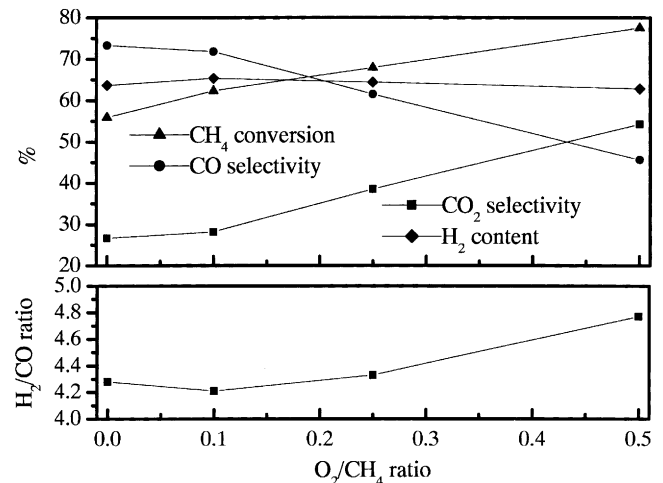


Fig. 6. Effect of O_2/CH_4 ratio on performance of catalyst for SRM and OSRM. Operating conditions: 1 atm; T , 650 °C; $\text{H}_2\text{O}:\text{CH}_4$, 1.0; GHSV, 7470 ml $\text{CH}_4/(\text{g}_{\text{cat}} \text{h})$.

observable deactivation, as shown in Fig. 5. Thus, from the above results and discussion, it can be concluded that $\text{Ni}/\text{Ce}-\text{ZrO}_2/\theta\text{-Al}_2\text{O}_3$ with high activity and stability is an efficient catalyst for SRM at low temperatures.

3.3. OSRM at low temperatures

The influence of $\text{O}_2:\text{CH}_4$ ratio in the feed at 650 °C and a fixed space velocity of 7470 ml $\text{CH}_4/(\text{g}_{\text{cat}} \text{h})$ on the conversion, selectivity and $\text{H}_2:\text{CO}$ ratio during SRM and OSRM is depicted in Fig. 6. When the $\text{O}_2:\text{CH}_4$ ratio is increased while maintaining a constant CH_4 flow rate and $\text{H}_2\text{O}:\text{CH}_4$ ratio of 1.0, it is found that CH_4 conversion increases markedly while O_2 is consumed to nearly 100%. Moreover, CO selectivity decreases significantly and hence the $\text{H}_2:\text{CO}$ ratio

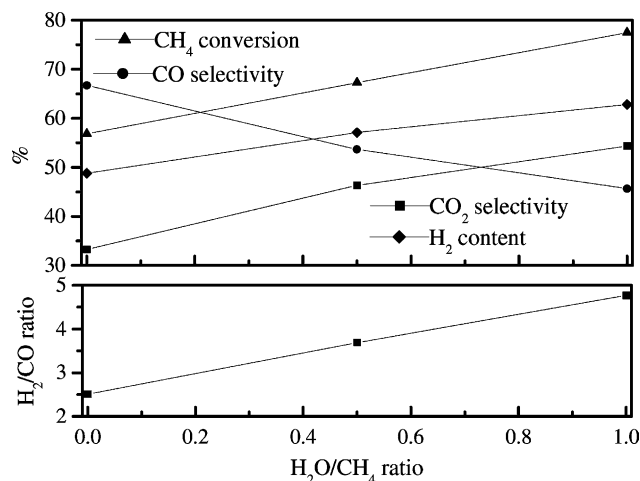


Fig. 7. Effect of H₂O/CH₄ ratio on performance of catalyst for POM and OSRM. Operating conditions: 1 atm; T, 650 °C; CH₄:O₂, 2.0; GHSV, 7470 ml CH₄/(g_{cat} h).

increases while the H₂ content in dry tail gas is almost constant. These observations clearly indicate that the POM reaction occurs simultaneously with the SRM and WGS reactions. The decrease in CO selectivity suggests that the rate of the WGS reaction increases with increasing O₂:CH₄ ratio.

The influence of H₂O addition in the feed on the conversion, selectivity and H₂:CO ratio for POM and OSRM at 650 °C and a fixed space velocity of 7470 ml CH₄/(g_{cat} h) is shown in Fig. 7. When there is no H₂O present in the feed, i.e. the POM reaction, CH₄ conversion is only about 56% (CH₄ conversion over the catalyst is about 90% for POM at 750 °C), while O₂ conversion approaches 100%. Moreover, the H₂:CO ratio (2.5) is higher than the stoichiometric value of 2.0 for POM. These observations suggest that complete oxidation of CH₄ occurs to an appreciable extent simultaneously with POM. With increase in H₂O:CH₄ ratio, both CH₄ conversion and H₂:CO ratio increase sharply which suggests that both the SRM and WGS reactions take place simultaneously in addition to the POM reaction. This is further confirmed by the significant decrease of CO selectivity with increasing H₂O:CH₄ ratio.

4. Conclusions

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 hydrogen production system through SRM for fuel cells at low temperatures is proposed by burning the unconverted CH₄ outside of the reformer to supply the energy for SRM. The calculated heat-balance temperature is 548 °C.
3. The Ni/Ce–ZrO₂/θ–Al₂O₃ catalyst shows very high activity and equilibrium CH₄ conversion and product distribution are approached at temperatures from 400 to 650 °C.
4. The Ni/Ce–ZrO₂/θ–Al₂O₃ catalyst has high stability without observable deactivation for 200 h during SRM at 650 °C.
5. CH₄ conversion increases significantly with increasing O₂:CH₄ or H₂O:CH₄ ratio, and the H₂ content in dry tail gas increases with H₂O:CH₄ ratio for OSRM at 650 °C.

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