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# Enhancement of hydrogen production rates in reformation process of methane using permeable Ni tube and chemical heat pump

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## ABSTRACT

Enhancement of the overall conversion efficiency from CH<sub>4</sub> to H<sub>2</sub> using a permeable-membrane Ni tube and temperature rise by a chemical heat pump system packed with hydrogen-absorbing alloys have been investigated in order to produce H<sub>2</sub> more efficiently using a high-temperature heat source. The two feasibilities to enhance the conversion efficiency are tested using their respective experimental apparatuses. Two things are experimentally proved that (1) Ni permeable-membrane tubes can provide measures to convert CH<sub>4</sub> to H<sub>2</sub> continuously without any deterioration in the course of partial oxidation or steam reformation and (2) two Zr(V<sub>1-x</sub>Fe<sub>x</sub>)<sub>2</sub> alloys with different Fe displacement ratios can comprise a chemical heat-pump system working at higher-temperature conditions.

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## Introduction

H<sub>2</sub> is an expected energy transmission media without any carbon emission during its burning in place of the present massive usage of oil. Its effective production is indispensable for wider H<sub>2</sub> usage through transport, storage and supply to fuel-cell vehicles or other energy conversion or generation devices as ultimate consumption. Finally, hydrogen will be produced without any carbon emission directly from H<sub>2</sub>O by using solar batteries or high-temperature heat sources such as high-temperature He gas-cooled fission reactors (HTGR) and the iodine–sulfur thermochemical cycle. However, it is unavoidable to use natural gas for H<sub>2</sub> generation in large quantities for the present, although HTGR is in preparation for resumption of service in Japan (HTTR) or China (HTR-10) after

Fukushima accident. Since natural gas fuel is used to produce H<sub>2</sub> by reformation processes, the reaction product of CO<sub>2</sub> should be recovered at the production site after fuel burning to generate high-temperature sources.

At present, several commercial on-site stations for H<sub>2</sub> production are available on the market, which are supplied with CH<sub>4</sub> and H<sub>2</sub>O, exhaust CO<sub>2</sub> and separately provide H<sub>2</sub> as a product. Each station is composed of a CH<sub>4</sub>–H<sub>2</sub>O reformer after desulfurization, a CO–H<sub>2</sub>O reformer using catalysts and a pressure-swing-adsorption (PSA) H<sub>2</sub> purifier. Since the first steam-reforming reaction proceeds around at 1000 K in case of Ni catalyst, these stations need high-temperature heat sources. The heat is supplied with burning fuels of CH<sub>4</sub> or other hydrocarbons. Therefore, it needs excess fuel consumption. It leads to a decrease of an overall CH<sub>4</sub>-to-H<sub>2</sub> conversion ratio. Although each process described above has already been

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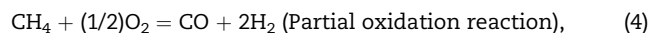
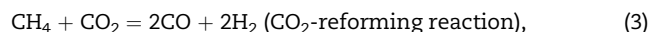
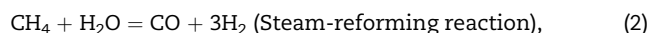
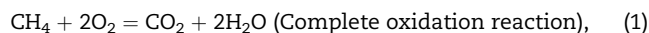
established technologically, high conversion ratio or efficient heat usage will lead to lower cost and consequently wider usage of H<sub>2</sub> as the major energy transmission measures when the overall efficiency of commercial H<sub>2</sub> production stations is raised.

Our research group of the energy chemical engineering laboratory in Kyushu University has been studying experimentally or analytically the following H<sub>2</sub>-related issues: (i) catalytic permeable-membrane tube reactor for steam-reformation or partial oxidation to convert CH<sub>4</sub> to H<sub>2</sub> effectively [1–3], (ii) chemical heat pump working at high-temperature heat conditions to raise efficiency of energy utilization [4–7], (iii) proton-conducting oxide fuel cells supplied with H<sub>2</sub> or CH<sub>4</sub> working at higher temperatures [8–11], (iv) adsorption of H<sub>2</sub> along with CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub> and other impurities on activated carbon at cryogenic temperatures around 20 K [12–15] and (v) a basic study to clarify some interactions between metals and hydrogen isotopes [16–19]. The first two issues (i)–(ii) are deeply related with the enhancement of the CH<sub>4</sub>-to-H<sub>2</sub> conversion ratio, effective utilization of high-temperature heat sources and direct energy conversion from CH<sub>4</sub> to electricity. Therefore, some results of our recent researches were presented in the ICH2P-2014 held in Kyushu University, and they are introduced in short in the present paper.

Our researches on enhancement of H<sub>2</sub> production efficiency focused here are categorized into clarification of the two feasibilities of (i) H<sub>2</sub> permeation through a Ni membrane without any deterioration under the conditions of the CH<sub>4</sub>-conversion temperature and concentration, and (ii) temperature increase by a chemical heat pump of Zr(V<sub>1-x</sub>Fe<sub>x</sub>)<sub>2</sub> working at the CH<sub>4</sub>-conversion temperature. The two feasibilities to enhance the conversion ratio are investigated using two kinds of experimental apparatuses. The results are discussed to clarify the possibility of enhancement of the conversion ratio from CH<sub>4</sub> to H<sub>2</sub> and efficient heat utilization by using a chemical heat pump packed with hydrogen-absorbing alloys.

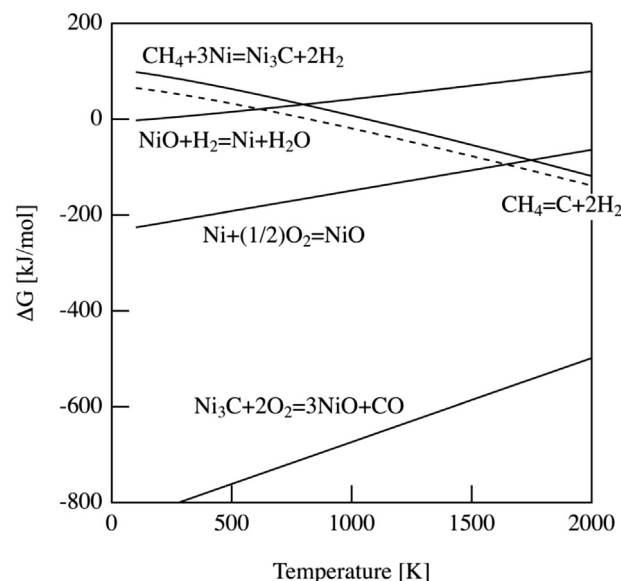
## Enhancement of H<sub>2</sub> production by its permeation

In this section, it is discussed whether or not permeable-membrane tube reactors can work under conditions of temperature between 673 and 1073 K and proper CH<sub>4</sub>/O<sub>2</sub> or CH<sub>4</sub>/H<sub>2</sub>O concentration ratio to produce H<sub>2</sub> from CH<sub>4</sub> effectively. In addition, it is investigated what kind material can work as the permeable membrane reactor under conditions of the CH<sub>4</sub>-reformation temperature and concentration of the partial oxidation or steam reforming. Several reactions are related with the CH<sub>4</sub>-to-H<sub>2</sub> conversion mechanism in the process of the partial oxidation or steam reforming. The following five overall reactions may proceed when CH<sub>4</sub> and O<sub>2</sub> or H<sub>2</sub>O is supplied to a membrane reactor:



Each equilibrium constant of (1)–(5) under constant pressure is defined as  $K_{p,i}$ ,  $i = 1-5$ . The names of their respective reactions are written in each bracket. Exhaust from a reaction chamber includes CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O before purification [1,3]. However, the above overall five reactions are not independent thermodynamically. For example, the overall equilibrium constants of the reactions (4) and (5) are expressed by  $K_{p,4} = (K_{p,1}K_{p,2}^2K_{p,3})^{1/4}$  and  $K_{p,5} = K_{p,2}/K_{p,3}$  using the first three equilibrium coefficients,  $K_{p,1}$ ,  $K_{p,2}$  and  $K_{p,3}$ . All the  $K_{p,i}$  values were calculated using the Gibbs free energy of formation for each component appearing in their respective reactions [3]. The values of the Gibbs free-energy changes,  $\Delta G_r$ , of the reactions (2) and (3) become negative when  $T > 900$  K and  $T > 920$  K, respectively. Therefore, the two reforming reactions proceed only at higher temperatures. The partial oxidation reaction (4) should proceed even at lower temperature judging from the Gibbs free-energy change, because of  $\Delta G_r < 0$  at any temperature. Previously, it was believed that the partial oxidation reaction does not proceed directly by the reaction (4) but by the two-step reactions of the complete oxidation (1) and then the two reforming reactions of (2) and (3). In the present paper, the two-step reaction model is adopted for analysis.

There are two candidate materials of Pd–Ag and Ni for permeable-membrane tube reactors. It is widely known that the intrinsic H<sub>2</sub> permeability of Pd–Ag alloy is much higher than that of Ni. Therefore, it is preferable to use Pd–Ag if no interaction or deterioration occurs on its surfaces. Several previous experiments showed Pd or Pd–Ag having good



**Fig. 1** – The Gibbs free-energy changes of the reactions between Ni<sub>3</sub>C or NiO and H<sub>2</sub>, O<sub>2</sub> or H<sub>2</sub>O.

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