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NOTE

Steam reforming of methane using a solar simulator controlled by $H_2O/CH_4 = 1/1$[†]

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The solar steam reforming of methane ($CH_4 + H_2O = CO + 3H_2$) on an Ni–Al_2O_3 catalyst has been investigated by maintaining the mole ratio of $H_2O/CH_4 = 1/1$ at 650, 750, 850 and 950 °C. The mole ratio of $H_2O/CH_4 = 1/1$ was adjusted throughout the reactions using a specially fabricated steam generator, where the desired relative humidity for a particular temperature in the methane gas stream was controlled by changing the CH_4 flow amount at atmospheric pressure. The stoichiometric steam content in the inlet gases of CH_4 and H_2O was adjusted by using a specially fabricated steam generator at atmospheric pressure. The reactor was irradiated with a concentrated xenon lamp as a solar simulator at each temperature. The gaseous contents in the outlet gases from the reactor were estimated from gas chromatography data. The amount of unreacted H_2O was calculated using the mass balance equations for atomic hydrogen and atomic oxygen by assuming that inlet gases of $CH_4 + H_2O$ produce outlet gases of CO, CO_2, H_2, CH_4 and H_2O, and deposition of carbon. The carbon deposition on the Ni–Al_2O_3 catalyst after reactions in the steam reforming of methane at a temperature above 850 °C were hardly detected by an elemental analyzer. On the other hand, the unreacted H_2O amount above 850 °C was less than 7 mol% among the outlet gases produced. The steam reforming of methane above 850 °C can reduce the unreacted H_2O and the carbon deposition, and maintain more than 85% of methane conversion efficiency by keeping $H_2O/CH_4 = 1/1$ under atmospheric pressure. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: solar energy; methane reforming; steam reforming; xenon lamp

INTRODUCTION

Storing solar energy in chemical reactions has received considerable attention by many researchers. The steam reforming of methane ($CH_4 + H_2O = CO + 3H_2$ $\Delta H = 206$ kJ mol^{-1}) has emerged as a favorite for consideration. This reaction is a well-known process for producing hydrogen in the chemical industry. Catalyst and process technologies are well documented.[1,2] In this reaction system a major concern is the large excess of steam (H_2O/CH_4 ratios from 2 to 3) necessary to prevent catalyst deactivation. Over 30% of the incident energy is consumed in generating this amount of steam. Unreacted, excess steam cannot be stored or transported but must be condensed at the endothermic stage. Böhmer *et al.*[3] and Rozenman[4] have investigated steam reforming using solar energy, and their investigations have been performed under conditions of high pressure and higher H_2O/CH_4 ratios than 1/1. In addition, they used an indirectly irradiated receiver, i.e. the heat transfer to the working fluid (*e.g.* the mixture of methane and steam) does not take place upon the surface that is exposed to incoming solar radiation. Instead, there is an intermediate wall, which is heated by the

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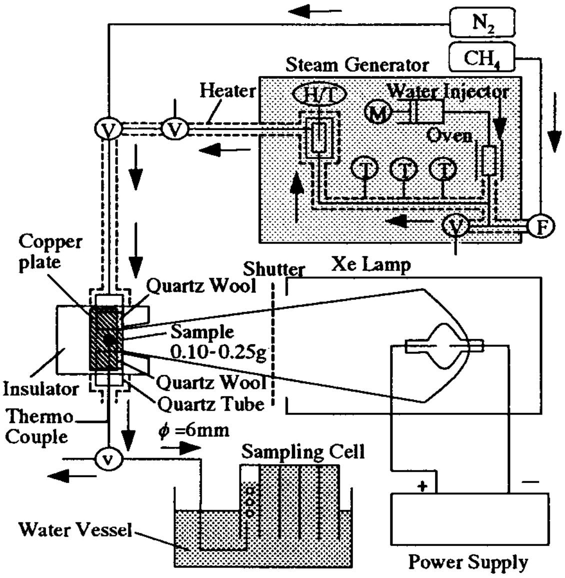

Figure 1 A schematic diagram of the apparatus.

irradiated sunlight on one side and transfers the heat to a working fluid on the other side. This receiver has some inherent weaknesses. The heat transfer requires large temperature differences. This, together with heat losses in the pipes, means that the energy is delivered at a much lower temperature than received. One of the keys to solving these problems is to use a directly irradiated receiver. No solar steam reforming of methane has been reported. A directly irradiated receiver is one where the heat transfer to the working fluid takes place upon the surface that is heated directly by the incoming radiation. Further, it would be interesting if the heat source contributed to methane steam reforming.

In this study, we investigated the solar steam reforming of methane on an Ni–Al_2O_3 catalyst, which was controlled to keep the stoichiometric mole ratio of $H_2O/CH_4 = 1/1$ using a xenon lamp as a light source (solar simulator) under atmospheric pressure.

EXPERIMENTAL

A nickel-on-alumina catalyst sample (23 wt% Ni) was prepared from $Ni(NO_3)_2{\cdot}6H_2O$ (0.28 g) and α-Al_2O_3 powder (7.0 g) by simple impregnation. A schematic diagram of the apparatus is shown in Fig. 1. It consisted of a gas delivery system with steam generator and a catalytic reactor. A mixture of methane and steam, whose ratio had been adjusted to 1:1 by keeping the humidity constant in the methane gas stream for a particular temperature, was passed through the reactor.[5] The reactor was irradiated by a 875–1755 W xenon arc lamp beam. The effluent gases were collected in a sampling cell and then were analyzed by gas chromatography equipment equipped with Porapak Q or Molecular Sieve 13X columns. The effluent gases passed through the water vessel contributed to eluting water from the chromatographic column. Since CO_2 is soluble in water, the amount dissolved with time is not negligible. In view of the time-course between sampling and analyzing the dissolved CO_2 amount was added to the CO_2 amount obtained by gas chromatography. The carbon deposited on the

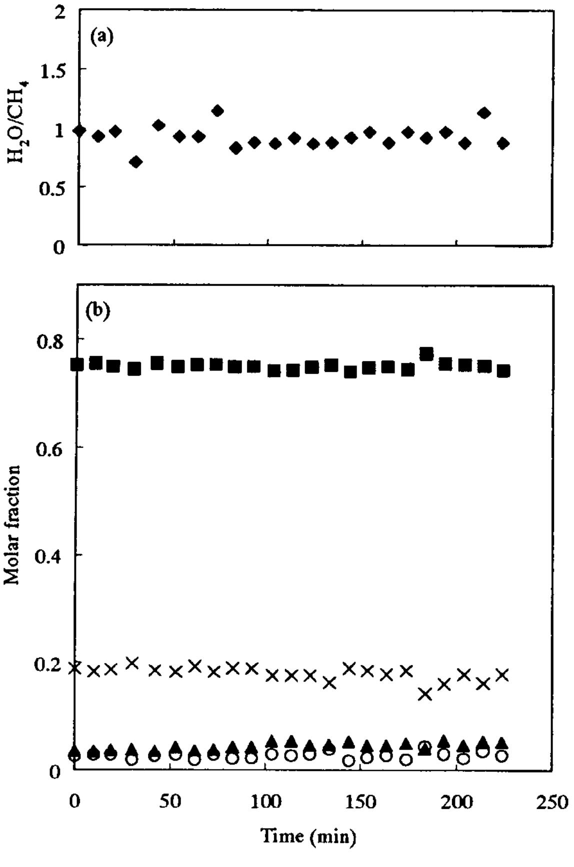

Figure 2 Time variation (a) in the mole ratio of inlet H_2O/CH_4 and (b) in the mole fraction of outlet H_2, CO, CO_2, CH_4 at 850 °C: ■, H_2; ▲, CH_4; ○, CO; ×, CO_2.

Table 1 The average compositions of inlet and outlet gases

	Xenon lamp				Electric furnace
	650 °C	750 °C	850 °C	950 °C	850 °C
Inlet H_2O/CH_4	1.0	1.1	0.9	1.1	1.1
Outlet (mole fraction)					
H_2	0.60	0.60	0.71	0.71	0.67
CH_4	0.13	0.09	0.04	0.03	0.04
CO	0.07	0.14	0.17	0.15	0.17
CO_2	0.06	0.02	0.03	0.04	0.02
H_2O	0.14	0.15	0.05	0.07	0.09
Carbon (wt%)	0.65	0.36	0.06	0.03	0.36
η (%)	61	70	85	90	84

η: methane conversion efficiency.

catalyst was analyzed using an elemental analyzer. We also investigated the steam reforming of methane at 850 °C by using an electric furnace.

RESULTS AND DISCUSSION

Figure 2 shows the time variation (a) in the mole ratio of inlet H_2O/CH_4 and (b) in the mole fraction of outlet H_2, CO, CO_2, CH_4 at 850 °C by gas chromatography. The mole ratio of H_2O/CH_4 was controlled to keep $H_2O/CH_4 = 1/1$ throughout this study using a specially fabricated steam generator. The unreacted H_2O amount was estimated by calculation.[5] The calculation was based on the assumption that the reaction of the CH_4 and H_2O inlet gases produces carbon, CO, CO_2, H_2, CH_4, and H_2O, and the mass balances before and after the reactions. Each mole fraction of the outlet gases was an almost constant value against time, as shown Fig. 2b. Table 1 shows the variation of the average H_2O/CH_4 and average molar fraction of outlet gases, the amount of deposited carbon and methane conversion efficiency through each experiment. Carbon deposition is one of the main factors in catalyst deactivation. Carbon deposition was hardly observed above 850 °C, as shown Table 1.

Böhmer *et al.*[3] and Rozenman[4] investigated solar steam reforming of methane using an inlet $H_2/O/CH_4$ mole ratio of 3/1 (under about 7 or 7.5 bar process gas pressure for Böhmer *et al.* and 20 atm for Rozenman). Böhmer *et al.* reported the unreacted H_2O amounted to be 29.8 mol% H_2O at 817 °C among outlet effluent gases of H_2, CO, CO_2, CH_4 and H_2O and Rozenman, 35 mol% at 515–815 °C. The unreacted H_2O at 850 °C will become lower than those values under their conditions, but will not be lower than 25 mol%.[3] The unreacted H_2O under the conditions of the present study was reduced by less than one-fifth of the value of Böhmer *et al.* The methane conversion efficiency was increased with increasing temperature (Table 1). The efficiency rose greatly between 750 and 850 °C and it became more than 85% above 850 °C.

The steam reforming of methane at 850 °C was also performed using an electric furnace as a heat source. The methane conversion efficiency was in agreement with that obtained by using the xenon lamp at 850 °C. However, the amount of deposited carbon by using the electric furnace was clearly detected by the elemental analyzer and unreacted H_2O was much greater. As with using sunlight, when using a xenon lamp a temperature gradient arises in the sample owing to the concentration of the light. Since the thermocouple was inside the sample, the temperature of thermocouple may indicate a lower value than that of the irradiated surface. To make the sample temperature as homogeneous as possible: (1) a thin quartz tube (6 mm diameter) was used, (2) a copper plate was rolled on the backside of the quartz tube, (3) the insulator was covered with the quartz tube except for the light aperture. If the reaction temperature for the xenon lamp and the electric furnace was the same, the difference in the outlet product will be due to the heat source. The xenon lamp may have the effect of depressing the production of carbon and H_2O, or the electric furnace may have the effect of accelerating the production of carbon and H_2O.

In this study, the carbon deposition and the unreacted H_2O were reduced by controlling $H_2O/CH_4 = 1/1$ and using a xenon lamp at atmospheric pressure. The key may be the use of a xenon lamp and a quartz tube, which enables the sample to be irradiated directly. We will study more exactly the effect caused by heating directly and indirectly.

REFERENCES

1. Van Hook JP. *Catal. Rev. Sci. Eng.* 1983; **21**: 1.
2. Rostrup-Nielsen JR. *Catalysis, Science and Technology*, vol. 5, Anderson JR, Boudart M (eds.). Springer-Verlag: Berlin, 1983; 1.
3. Böhmer M, Langnickel U, Rodriguèz JA, Sánchez M, Valverde A. *Proceeding of the 6th International Symposium on Solar Thermal Concentrating Technologies*, Mojacar, Spain, 1992; 987–995.
4. Rozenman JF. *J. Solar Energy Eng. Trans. ASME* 1987; **109**: 221.
5. Yokota O, Oku Y, Sano T, Hasegawa N, Matsunami J, Tamaura Y. *Int. J. Hydrogen Energy* 2000; **25**: 81.