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Short communication

Fast start-up reactor for partial oxidation of methane with electrically-heated metallic monolith catalyst

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Abstract

A palladium-washcoated metallic monolith catalyst is applied to the partial oxidation of methane to syngas. This catalyst is highly active at a gas hourly space velocity (GHSV) of 100,000 h^{-1}. The compact partial oxidation (POX) reactor equipped with both 96 cc of the metallic monolith catalyst and an electrically-heated catalyst (EHC) has a start-up time of less than 1.5 min and a syngas generation capacity of 9.5 Nm^3 h^{-1}. The POX reaction is sustained without the need for an external heater. With the stand-alone POX reactor, the methane conversion can be increased either by preheating the reactant mixture heat-exchanged with the product gas, or by supplying a larger amount of oxygen than is necessary for the reaction stoichiometry.
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1. Introduction

Steam reforming (SMR), partial oxidation (POX) and autothermal reforming (ATR) are the major technologies to produce hydrogen from hydrocarbon fuels [1]. Among them, SMR is regarded to be the most efficient. Nevertheless, it has been recently argued that catalytic POX and ATR could be more efficient than SMR [2]. In addition to a high efficiency, catalytic POX reforming has the other advantages of compactness, fast start-up, and a good load-following behaviour. Both small-scale fuel cells and fuel cells for mobile applications demand a compact fuel processor with a fast start-up capability [3]. Thus, catalytic POX reforming is the preferred component of the fuel processor to supply hydrogen for such fuel cell applications [4].

This study reports the development of a compact catalytic POX reactor which is equipped with both a metallic monolith catalyst and an electrically-heated catalyst (EHC) for fast start-up. The catalyst provides the advantages of low pressure drop and resistance to thermal shock. The detailed operation and the start-up characteristics of the POX reactor are described.

2. Experimental

Palladium and ruthenium were selected as candidates for the high efficiency POX catalyst. The catalysts were prepared in a washcoated form on a metallic monolith. The monolith was prepared by winding a combination of a flat plate and a wave-form plate (50 μm thickness, Fecralloy from Goodfellow Co.). The monolith thus obtained had a cell density of about 640 cpi. The monolith was pre-oxidized to enhance the adhesive force between the ceramic-type washcoated catalyst and the metal monolith. Cylindrical metallic monolith catalysts were prepared in two different sizes, namely: 2 cm (diameter) × 2 cm (height), and 3.5 cm (diameter) × 2 cm (height).

A highly concentrated slurry of fine particles of the calcined product of alumina and cerium acetate was prepared and the appropriate amount of palladium nitrate or ruthenium nitrate was dissolved in the slurry. Metallic monoliths were dipped in the slurry and dried at room temperature several times until the desired amount of the catalyst was washcoated. The dried monolith was calcined in air with a temperature programmed to increase up to 900 °C. The amount of the washcoated catalyst was 0.16 g cm^{-3} of the monolith. The amount of the impregnated novel metals was 4 wt.% of the washcoat.
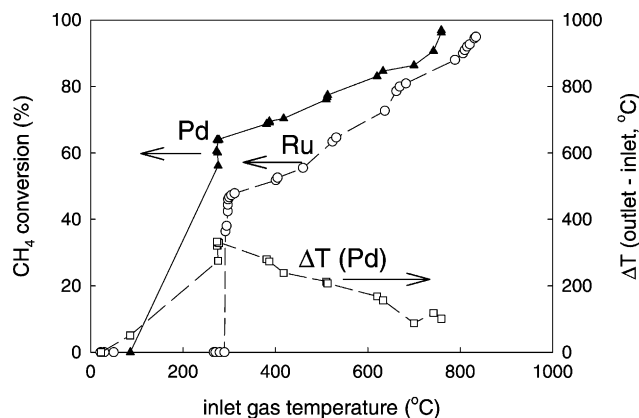
Fig. 1. Temperature-programmed partial oxidation of methane over Pd- or Ru-washcoated metallic monolith catalysts (O$_2$ in air:CH$_4$ = 0.55, GHSV = 19,000 h^{-1}; catalyst volume: 12.6 cc).

The electrically-heated catalyst was prepared by welding electrical rods at both ends of the metallic monolith which was pretreated to prevent short-circuits. Palladium was washcoated on the EHC in the same way as the monolith catalyst.

Two reactors of different size were employed to test the POX reaction, namely: a quartz reactor with an inside diameter of 2.1 cm, and a stainless-steel reactor with an inside diameter of 5.1 cm. The quartz reactor was heated by an electrical furnace. The stainless-steel reactor was not equipped with an external heater but used the internal EHC to initiate the POX reaction.

The reactants were methane and air; the flow rates were controlled by mass-flow controllers (Brooks, 5850E). The ratio of O$_2$:CH$_4$ was maintained at 0.5–0.7. A dry gas meter installed at the exit of the reactor was used to measure the flow rate of the product gas. A gas chromatograph equipped with a Porapak Q column and a mass spectrometer (PRISMA, Pfeiffer Vacuum) were used to analyze the composition of both the reactant and the product gases. Based on the flow rate and the composition of the product gas, the conversion and the selectivity were calculated.

3. Results and discussion

3.1. Catalyst screening

The temperature-programmed POX reaction was carried out over the metallic monolith catalysts with the novel metal washcoat (two 2 cm × 2 cm sized catalysts, 12.6 cc). The reaction was run at a gas hourly space velocity (GHSV) of 19,000 h^{-1}. The change in methane conversion with inlet gas temperature is shown in Fig. 1. The GHSV was defined as the ratio of the reactant gas flow rate at 20 °C and 1 atm to the total volume of the catalyst. The inlet gas temperature was measured at 4 cm above the catalyst. The space between the catalyst and the thermocouple was filled with the metal-

lic monolith without the catalyst washcoat for even distribution of the reactant gas. The data in Fig. 1 show that the reaction started at a slightly lower inlet gas temperature over the Pd-washcoated catalyst than over the Ru catalyst. The Pd catalyst also gave a higher CH$_4$ conversion than the Ru catalyst at the same inlet temperature. Once the POX reaction started, the catalyst exit temperature became higher than the inlet gas temperature due to the exothermic heat of the reaction. For example, the exit gas temperature from the Pd catalyst was 330 °C higher when the inlet gas temperature was 276 °C. The temperature difference between the inlet gas and the exit gas from the Pd catalyst is also shown in Fig. 1.

In a study by Bhattacharya et al. [5], Pd catalysts on various support materials were reported to be active for the methane partial oxidation reaction. Mouaddib et al. [6] also reported that Pd/Al$_2$O$_3$ was active for both the partial oxidation and the steam reforming of methane. By contrast, Torniainen et al. [7] reported that a Pd catalyst supported on a ceramic monolith displayed only a moderate activity for methane partial oxidation and became deactivated due to coke formation. The authors also carried out methane partial oxidation over a Ru catalyst and found out that the reaction did not proceed [7]. Contrary to these results, both the Pd catalyst and the Ru catalyst washcoated on the metallic monolith in the present study show high activities for methane partial oxidation. Ceria in the support material could be the reason for this high activity.

Torniamen et al. [7] claimed that the POX reaction could be ignited only when the CH$_4$–air mixture was heated above 600 °C. We observe, however, that the POX reaction is initiated when the temperature of the CH$_4$ and air mixture is about 270 °C over both the Pd-washcoated metallic monolith catalyst and the Ru catalyst (Fig. 1). Thus, the ignition temperature for the POX reaction of methane appears to depend on the activity of the catalyst with the reaction starting at lower temperatures over the more active catalyst. Kikuchi et al. [8], also reported that the total oxidation of methane ignited at a lower temperature over the monolith catalyst with a higher Pd washcoat loading.

3.2. Effect of GHSV and inlet gas temperature

The flow rate of the reactant gas entering the quartz reactor (inside diameter of 2.1 cm) with 12.6 cc of the Pd-washcoated monolith catalyst was varied. The effect of the GHSV on the conversion of CH$_4$ is shown in Fig. 2. The furnace temperature was maintained at 800 °C and the catalyst exit temperatures were between 835 and 850 °C. At GHSVs of 47,000 and 108,000 h^{-1}, the CH$_4$ conversion is higher than 90%. On the other hand, the CH$_4$ conversion is only 60% at a GHSV of 240,000 h^{-1}. Based on the results in Fig. 2, the safe range of GHSV for high CH$_4$ conversion over the Pd-washcoated monolith catalyst is estimated to be less than 100,000 h^{-1}.

The temperature profiles during the start-up and course of the POX reaction over the Pd-washcoated monolith catalyst
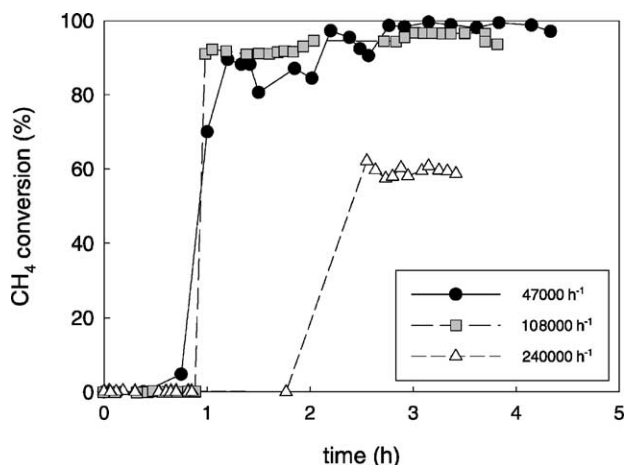
Fig. 2. Partial oxidation activity of Pd metallic monolith catalysts at different space velocities (O$_2$ in air:CH$_4$ = 0.55; catalyst exit temperature = 835–850 °C; catalyst volume: 12.6 cc).

at a GHSV of 108,000 h^{-1} are presented in Fig. 3. As also shown in Fig. 1, the reaction starts at a gas inlet temperature of about 270 °C and the temperature after the catalyst increases suddenly to 700 °C due to the exothermic heat of the POX reaction. Once the reaction commenced, the electricity supply to the external furnace was terminated and one-half of the furnace was removed. Thus, one-half side of the reactor was exposed to the atmosphere at room temperature. As can be seen in Fig. 3, the inlet gas temperature gradually decreases due to the absence of a heat supply from outside. Nevertheless the POX reaction continues to take place, even when the inlet temperature is dropped to 200 °C. Although the reactant gases are fed to the reactor at the room temperature, the inlet gas temperature measured by a thermocouple is higher due to the heat transferred from the catalyst.

The results in Fig. 3 further indicate that once the POX reaction starts over the Pd-washcoated monolith catalyst, the reaction can be sustained without the supply of external
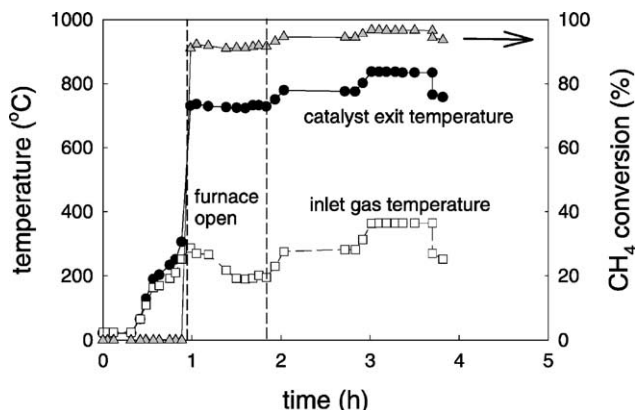

Fig. 3. Effect of inlet gas temperature on methane conversion and outlet temperature during partial oxidation of methane over Pd metallic monolith catalysts (O$_2$ in air:CH$_4$ = 0.55; GHSV = 108,000 h^{-1}; catalyst volume: 12.6 cc).

heat. The self-sustaining behaviour of the POX reactor is probably due to the high heat transfer property of the metallic monolith catalyst [9,10]. The highly conductive nature of the metal catalyst would facilitate the transfer of reaction heat from the bottom part to the front part of the catalyst where the cold inlet gas continuously removes the heat. Thus, the heat transferred from the bottom raises the temperature of the cold gas instantaneously and can therefore prevent blowout of the reaction. Hohn and Schmidt [11] also suggested that a catalyst geometry with a higher heat transfer capability can prevent blowout of the POX reaction at high space velocities. The above finding is important in designing a compact POX reactor since the reactor only needs a reaction-initiating device without an external heater.

It should be pointed out that the conversion of CH$_4$ is about 90%. Since the reaction is carried out in a near adiabatic mode with the reactant gas fed at room temperature, the heat of the reaction can raise the temperature of the product gas to only about 700 °C.

The inlet gas temperature was varied using the external heater and its effect on the CH$_4$ conversion and the temperature after the catalyst is also shown in Fig. 3. As can be seen, increase in the inlet gas temperature results in an increase in both the outlet temperature and the CH$_4$ conversion. When the inlet gas is preheated to temperatures above 300 °C a CH$_4$ conversion of higher than 95% is observed. This is the expected result in that the preheated reactant gas increases the reaction temperature, which raises the equilibrium conversion of methane. Since the outlet gas temperature can be maintained at about 700 °C, an efficient heat exchanger installed at the exit of the reactor can raise the temperature of the inlet gas above 300 °C to improve the conversion.

3.3. Fast start-up with EHC

Five cylindrical monolith catalysts (3.5 cm diameter and 2 cm height; total volume 96 cc) were charged into a stainless-steel reactor with an inside diameter of 5.1 cm. The total volume of the reactor shown in Fig. 4 was 1140 cc. The space between the catalyst and the reactor wall was filled with high temperature insulation to minimize heat loss. An EHC with a Pd-washcoat was installed in front of the catalyst bed for start-up of the POX reaction. This stand-alone reactor was not equipped with an external heater but with thermal insulation. The reactant gas flow rate was maintained at 71.5 l min^{-1} (O$_2$:CH$_4$ = 0.553; GHSV = 44,700 h^{-1}) and 30 V of electricity was supplied to the EHC. As shown in Fig. 5, within 1.5 min of the electricity supply the outlet gas temperature increased to 580 °C, which indicated that the POX reaction had started. Once the POX reaction was initiated, the electricity supply to the EHC was cut off. The reaction went on without heating from the EHC. The initial CH$_4$ conversion was 80%. As the time on stream increased, both the inlet temperature and the outlet temperature gradually increased due to slow warming of the entire reactor. The CH$_4$ conversion also
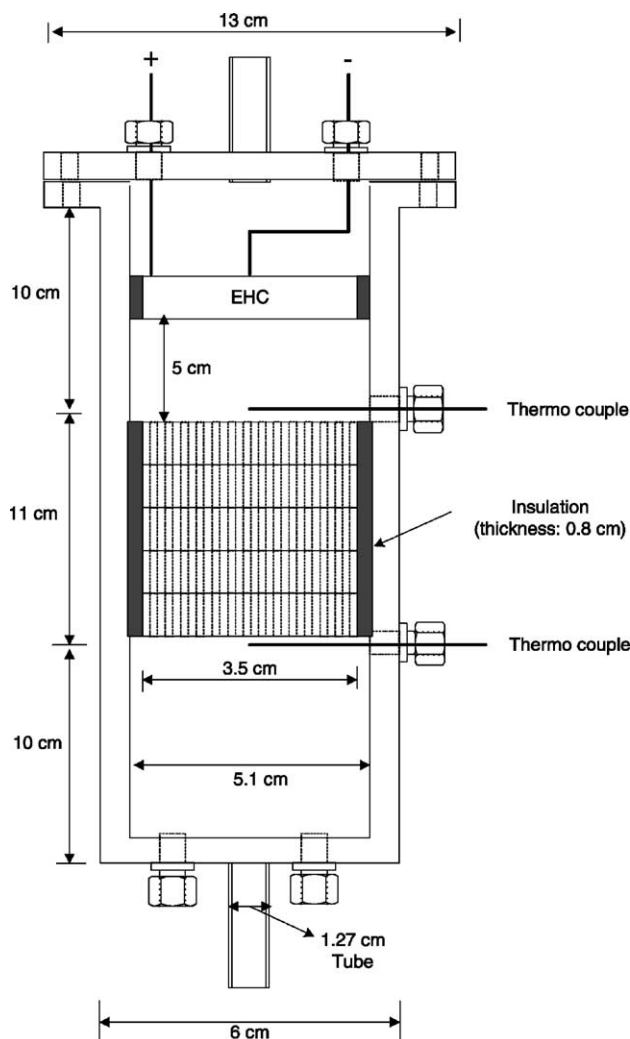
Fig. 4. Schematic diagram of compact stainless-steel reactor equipped with both EHC and 96 cc of Pd-washcoated metallic monolith catalyst.

increased with temperature. At a steady-state temperature of 668 °C, the CH_4 conversion was 86.1% with H_2 and CO selectivity of 82.3 and 85.0%, respectively. In a separate run with the EHC without the Pd-washcoat, the start-up of the
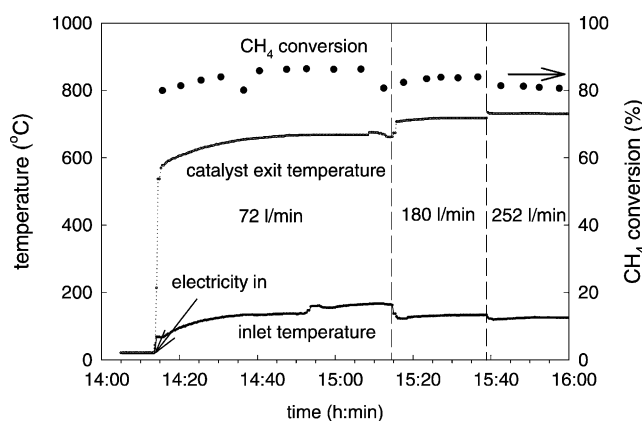

Fig. 5. Start-up behaviour of POX reactor equipped with EHC and Pd metallic monolith catalysts with reactant gas fed at room temperature.

reaction took place within 8 min of the electricity supply. In that case, the EHC was functioning only as an internal heater. Once the catalyst was heated to about 270 °C by the hot reactant gas, the POX reaction was initiated. Thus, the effectiveness of the Pd-washcoated EHC as a start-up device was clearly manifested.

Other methods of igniting the POX reaction reported in the literature are: (i) heating a NH_3–air mixture with a burner, this ignites NH_3 combustion over the catalyst which raises the temperature of the catalyst above 600 °C and then the $CH_4:O_2$ mixture is fed to the catalyst [7]; (ii) a sparker to ignite the complete combustion of CH_4 to heat the catalyst to about 600 °C and then the reactant at a stoichiometric ratio of $CH_2:O_2$ is introduced [12]. The second method demonstrated that ignition of the methane POX reaction took less than 10 s with 2.5 cc of an alumina foam monolith catalyst [12]. It should be noted, however, that the use of spark-ignited complete combustion as the start-up method may pose a danger of explosion.

During the reaction, step increases of the flow rate of the reactant gas were made and the results are also shown in Fig. 5. As the inlet gas flow rate is increased to 189 and 270 l min^{-1}, a slight decrease in CH_4 conversion is observed from 86.1 to 83.8 and 81.0%, respectively. The syngas production increases almost linearly and instantaneously upon change of the inlet gas flow rate. In this run, the maximum flow rate of the syngas generated from the reactor charged with 96 cc of the Pd-washcoated metallic monolith catalyst is 9.5 Nm^3 h^{-1}.

It should be pointed out that ceramic monolith catalysts, which undergo rapid temperature change such as the metallic ones in the above POX reactor, are prone to cracks due to thermal shock. The metallic catalysts subjected in this work are very resistant to thermal shock and maintain their physical structure after repeated temperature cycles. In addition, their conductive nature can minimize the formation of hot spots [13].

3.4. $O_2:CH_4$ ratio

As discussed previously, the stand-alone POX reactor operated in an adiabatic mode shows limited CH_4 conversion since the temperature of the reaction medium which entered the reactor at room temperature was raised only by the heat of the reaction. More oxygen than is necessary for the POX reaction in the reactant gas is required to promote the complete combustion of methane, H_2 or CO. The heat generated from the parallel complete combustion should raise the temperature of the overall reaction and lead to higher CH_4 conversion.

The POX reaction was carried out with various flow rates of air while maintaining the CH_4 flow rate constant at 19.7 l min^{-1}. The results are listed in Table 1. As expected, the increase in both the CH_4 conversion and the temperature at the exit of the catalyst bed was observed at the higher $O_2:CH_4$ ratio. At a ratio of 0.7, almost complete conversion

Table 1
Effect of O_2:CH_4 ratio on conversion and selectivity (CH_4 fed at $19.71 \, min^{-1}$ over 96 cc of Pd-washcoated metallic monolith catalyst)

O_2:CH_4	Temperature at exit of catalyst bed (°C)	CH_4 conversion (%)	H_2 selectivity (%)	CO selectivity (%)	H_2 yield (%)
0.51	603	78.8	81.0	84.4	63.8
0.55	618	84.7	81.7	84.2	69.2
0.60	654	89.0	80.0	83.4	71.2
0.65	684	94.6	79.2	83.4	74.9
0.70	724	98.9	77.6	83.4	76.7

of CH_4 is observed, even though the reactant gas mixture is fed to the reactor at the room temperature. The excess amount of oxygen is consumed by combusting H_2 and CO. The selectivity of H_2 decreases slightly as the O_2:CH_4 ratio is increased, while the CO selectivity remains almost constant. By contrast, the yield of hydrogen (CH_4 conversion times H_2 selectivity) increases significantly with the O_2:CH_4 ratio, which indicates that larger amounts of H_2 can be extracted from CH_4 by feeding excess amounts of air.

4. Conclusions

The partial oxidation of methane to syngas has been carried out in a reactor charged with both a Pd-washcoated metallic monolith catalyst and an electrically-heated catalyst (EHC). The former catalyst is active at high space velocities up to $100{,}000 \, h^{-1}$. The stand-alone type reactor has a start-up time of less than 1.5 min with the reactant gas fed to the reactor at the room temperature. The syngas generation capacity of the Pd catalyst is 10 cc per $1 \, Nm^3 \, h^{-1}$ of syngas. The near complete conversion of methane can be accomplished with the developed reactor either by pre-heating the reactant gas or by mixing excess amounts of oxygen (air) compared with the stoichiometrically required amount.

References

[1] A. Heinzel, B. Vogel, P. Hubner, J. Power Sources 105 (2002) 202.
[2] S. Ahmed, M. Krumpelt, Int. J. Hydrogen Energy 26 (2001) 291.
[3] S.S. Bharadwaj, L.D. Schmidt, J. Catal. 42 (1995) 109.
[4] V. Recupero, L. Pino, R.D. Leonardo, M. Lagana, G. Maggio, J. Power Sources 71 (1998) 208.
[5] A.K. Bhattacharya, J.A. Breach, S. Chand, D.K. Ghorai, A. Hartridge, J. Keary, K.K. Mallick, Appl. Catal. 80 (1992) L1.
[6] N. Mouaddib, C. Feumi-Jantou, E. Garbowski, M. Primet, Appl. Catal. A 87 (1992) 129.
[7] P.M. Torniainen, X. Chu, L.D. Schmidt, J. Catal. 146 (1994) 1.
[8] R. Kikuchi, S. Maeda, K. Sasaki, S. Wennerstrom, Y. Ozawa, K. Eguchi, Appl. Catal. A: Gen. 239 (2003) 169.
[9] A. Cybuiski, J. Moulijn, Chem. Eng. Sci. 49 (1994) 19.
[10] G. Groppi, E. Tronconi, Chem. Eng. Sci. 55 (2000) 2161.
[11] K.L. Hohn, L.D. Schmidt, Appl. Catal. A: Gen. 211 (2001) 53.
[12] L.D. Schmidt, E.J. Klein, C.A. Leclerc, J.J. Krummenacher, K.N. West, Chem. Eng. Sci. 58 (2003) 1037.
[13] I. Yuranov, N. Dunland, L. Kiwi-Minsker, A. Renken, Appl. Catal. B: Environ. 36 (2002) 183.