

Temperature Profiles of the Monolith Catalyst in CO₂ Reforming of Methane with *in-situ* Combustion of Methane and Ethane

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Abstract—The temperature profiles in a monolith reactor were measured in CO₂ reforming of CH₄ with *in-situ* combustion of methane and ethane in order to find out in what sequence the reactions are occurring. The reaction gas flowed both upward and downward. A hot spot was observed at low furnace temperatures, and it tended to disappear as the furnace temperature increased. This is due to natural extinguishment of the flame caused by the endothermic reforming reactions occurring. The hot spot disappeared at a lower temperature with the up-flow when compared with the down-flow. When the hot spot appears, H₂O and CO₂ are produced by complete oxidation and accordingly the steam reforming and the CO₂ reforming occur competitively in the rear part of the monolith. If the hot spot does not appear, it is considered that the partial oxidation of methane occurs predominantly over the complete oxidation, resulting in more efficient CO₂ removal.

Key words: Carbon Dioxide Reforming, *in-situ* Combustion, Methane, Monolith, Temperature Profile

INTRODUCTION

Recently, the interest in CO₂ reforming of CH₄ has rapidly increased for both environmental and economic reasons. Both CO₂ and CH₄ are the most abundant and cheapest carbon-containing gases, but these gases are considered as harmful greenhouse gases [Gavin and Bower, 1991; Edwards, 1995; Kilaparti, 1997; Souza et al., 2001; WMO, 2000]. The advantages of the reforming are disposing and recycling these gases; if the CO₂ reforming of CH₄ or dry reforming is used, a decrease of the CO₂ emission and simultaneous production of a synthesis gas can be achieved so that the carbon resource can be recycled [Asami et al., 2003; Ashcroft et al., 1991; Edwards, 1995; Edwards and Maitra, 1995]. By the way, the reforming of methane only with CO₂ is a highly endothermic reaction, and hence external heat supply is inevitable. This causes another problem that CO₂ is emitted from another place. One solution to such a problem is to feed O₂ together with more CH₄ so that *in-situ* combustion of a part of CH₄ in the reactor may supply the heat necessary. This will prevent lowering of the reactor temperature or minimize the external heat supply [Ashcroft et al., 1991; Rostrup-Nielsen, 1994; Vernon et al., 1992]. Thus, a complex external heating apparatus may be omitted or it can become more compact. In addition, H₂O and CO₂ produced by CH₄ combustion can be subsequently converted *in situ* to CO and H₂ by the reforming reactions with CH₄. Consequently, the emission of CO₂ becomes significantly smaller. At the same time, conversion of H₂O into CO and H₂ by the steam reforming of methane results in increase of the H₂/CO ratio, since the H₂/CO ratio of the syngas by the steam reforming is 3 while that by the CO₂ reforming is 1. Adjustment of the H₂/CO ratio is also possible to some extent, and therefore the

produced gas has more flexible applications for the next synthesis processes.

A few studies about temperature profiles related with this work have appeared in the literature. Inui and coworkers [1997] have reported as follows: four components of Ni-Ce₂O₃-Pt-Rh were supported on the alumina-coated ceramic fibers. The fibers were formed into a plate shape of 1 mm thickness and the reactions were carried out over this catalyst. In case of *in-situ* combustion of ethane or propane with oxygen and with the CH₄/CO₂ ratio of 1, the catalyst bed temperature was observed to be higher by about 200 K than the furnace temperature. Consequently, even if the furnace temperature was low (as low as 623 K), the CH₄ conversion was quite high. However, since the feed ratio of CH₄/CO₂ was 1, the CO₂ produced by the combustion of ethane or propane was not effectively eliminated. When the feed ratio of CH₄/CO₂ was 3.5, the CO₂ produced by combustion was substantially eliminated. However, the difference of the temperature between the furnace temperature and the catalyst bed temperature was not disclosed. So it was not known whether the catalyst bed temperature was higher or lower than the furnace temperature. The temperature was measured at only one position, and the position where the temperature was measured was not described exactly. In another work, Tomiainen and coworkers [1994] carried out exothermic partial oxidation of CH₄ over a monolith, which was prepared by coating several metals. They observed large temperature rises in the monolith compared with the feed gas temperature, but they did not measure the temperature profiles along the position through the monolith.

When the combustion of hydrocarbons and CO₂ reforming of methane occur together in one reactor, it is not known whether combustion occurs first and is followed by reforming, or both reactions occur together. Also, it has not been well known whether the sequence of such reactions may be influenced by the reaction conditions. In addition, there have been few works on the examination of temperature profiles in a monolith catalyst. Examination of the temperature profiles could be helpful to assess two debatable mech-

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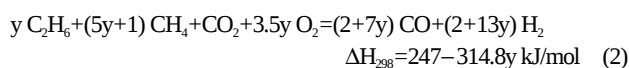
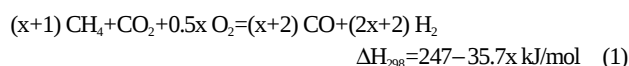
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anisms for partial oxidation of methane: one is the two-step mechanism, where the complete combustion occurs first and then the steam and CO₂ reforming follow, and the other is the methane-decomposition (or pyrolysis) mechanism. In case of the former, a hot spot will appear near the inlet of the bed and the temperature in the rear part of the bed will be lowered significantly [Kim et al., 2003]. Dissanayake et al. [1991] reported observation of the hot spot and suggested a two-step mechanism, but did not measure the temperature profile. In case of the latter mechanism, observation of the hot spot may not be expected but the entire bed temperature will be moderately higher than the furnace temperature.

If the shape of the catalyst is powder or pellet, it is not easy to obtain a temperature profile of the catalyst bed. But if the shape of the catalyst is a monolith of honeycomb, it is relatively easy to measure the temperature profile by moving the thermocouple up and down. In this work, the temperature profile along the position was examined by using such shape of a catalyst. The reactions occurring were CH₄ combustion-CO₂ reforming of methane and the C₂H₆ combustion-CO₂ reforming of methane. (5)CeO₂-(10)Ni-(1)Pt/Al₂O₃ catalyst powder, which has been reported to show good catalytic performance for the CH₄ combustion-CO₂ reforming [Kong, 2002; Kong et al., 2002], was used as the washcoat of the monolith. By doing so, we investigated in what sequence the reactions were occurring. In addition, the reacting gas was flowed both upward and downward and the differences were compared. It was also discussed whether the released heat from the combustion could effectively be used for the reforming reactions or not.

THERMOCHEMICAL CONSIDERATIONS

In this reaction system, various reactions can occur. Thermochemical data for these have appeared in a previous article [Kong et al., 2002]:



If an ideal reaction as shown by Eq. (1) for the removal of CO₂ proceeds to produce only CO and H₂ as the final products, the CH₄ combustion-CO₂ reforming of CH₄ becomes overall exothermic when x is larger than 7. In this case, the H₂/CO ratio becomes 16/9 (=1.78). If the C₂H₆ combustion-CO₂ reforming of CH₄ proceeds ideally as shown by Eq. (2), it becomes overall exothermic when y is greater than 0.75, where the H₂/CO ratio becomes 11.75/7.25 (=1.62). Therefore, the syngas produced by these reactions will have wider applications than that produced by only CO₂ reforming of CH₄ (H₂/CO=1). But in reality, the CH₄ conversion is limited and the CO₂ cannot be removed completely owing to the chemical equilibrium as well as limited reaction rates.

EXPERIMENTAL

1. Preparation of the Monolith Catalyst

The (5)CeO₂-(10)Ni-(1)Pt/Al₂O₃ powder catalyst was prepared by dry impregnation (incipient wetness method) of the support with

nearly saturated solutions of the corresponding precursors [Kong, 2002; Kong et al., 2002]. The support used was γ -alumina (Strem Chemicals, 1/8 inch cylindrical pellets). It was crushed and sieved to get 40-to-80-mesh powder and then dried in air at 673 K for 2 h. The precursors used were chloroplatinic acid (H₂PtCl₆·xH₂O, Aldrich Chem., assay 40% Pt), Ni(NO₃)₂·6H₂O (Shinyo Pure Chem., Assay 97%), and cerium nitrate (Ce(NO₃)₃·6H₂O, Yakuri Pure Chem., assay 98%). The precursors were impregnated stepwise in the order of CeO₂, Ni and Pt. After impregnation of each precursor, the powder was dried at 383 K for 12 h and calcined at 773 K for 4 h.

A honeycomb support was used to prepare the monolith catalyst. The honeycomb is made from cordierite (2Al₂O₃·2MgO·5SiO₂) with channels of square cross section, and the cell density is 400 cpsi (cells per square inch). The honeycomb was cut so that the monolith had 17 cells, the length of 28 mm, and the diameter of ca. 8 mm. Four walls of the cells at the center of the monolith were removed in order that a 1/16-inch (1.6 mm) thermocouple could be inserted. The weight of the monolith before the washcoating was about 0.44 g. In order to use as the washcoat, the (5)CeO₂-(10)Ni-(1)Pt/Al₂O₃ powder was again crushed into fine particles (below a few tens of micrometers). The fine powder was suspended in water, and the washcoated monolith catalyst was prepared by repeated dipping into the suspension. After each dipping, it was dried at 373 K for 12 h and calcined at 673 K for 2 h in air. This step was repeated until the net weight of the coated powder catalyst became approximately 0.08 g.

2. Reaction Experiments

The reaction was carried out in a conventional flow-type, vertical tubular reactor made of quartz. The inside diameter of the reactor was 8 mm and the middle of the tube was heat-treated to be narrowed somewhat so that the monolith could be placed on there (Fig.

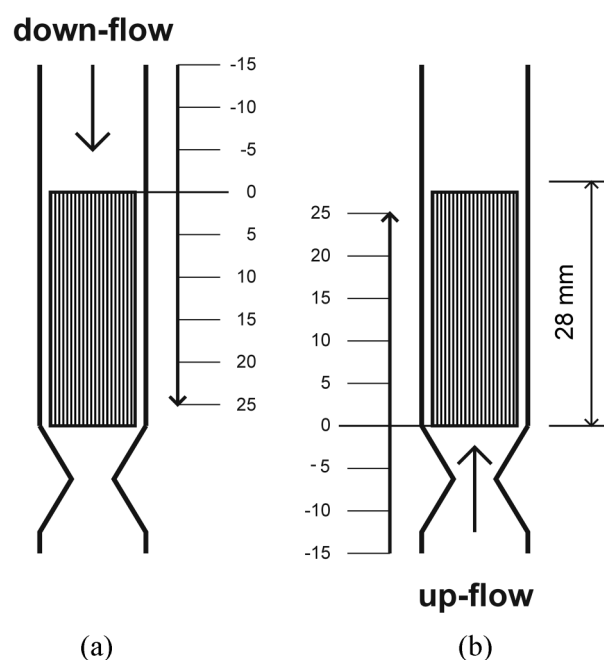


Fig. 1. Thermocouple position in the monolith reactor for temperature profile measurement with (a) down-flow and (b) up-flow of the gas.

1). The monolith catalyst was reduced *in situ* at 973 K for 2 h with pure hydrogen flow. The reaction temperature was controlled with an external electric furnace.

The reactant gases (CH₄, C₂H₆, O₂, CO₂) were fed via mass flow controllers and argon was used as the diluent. The effluent gas from the reactor was analyzed by a gas chromatograph (GC) equipped with a TCD detector (Younglin M600D) and a Carboxen 1004 column (Supelco). In the CH₄ combustion-CO₂ reforming of CH₄, the feed compositions of CH₄ : O₂ : CO₂ : Ar were 20 : 5 : 10 : 65 ($x=1$) and 32 : 14 : 4 : 50 ($x=7$). In the C₂H₆ combustion-CO₂ reforming of CH₄, the feed composition of CH₄ : C₂H₆ : O₂ : CO₂ : Ar was 37.5 : 4.5 : 15.75 : 15 : 27.25 ($y=0.3$). The total flow rate of the reactant gases was 100 cm³ (STP)/min. The reaction was carried out both with down-flow and up-flow of the gas. During the reaction, the temperatures in the reactor, including the inside of the monolith, were measured at several positions by using the inserted thermocouple. The thermocouple could be moved up and down with negligible leaking by slightly loosening the nut with a Teflon ferrule.

RESULTS AND DISCUSSION

1. CH₄ Combustion-CO₂ Reforming of CH₄

The temperature profiles in the reactor with a monolith catalyst were measured in the CH₄ combustion-CO₂ reforming of CH₄, and the results are shown in Figs. 2-5. The measured temperatures in the reactor during the reaction were compared with the furnace tem-

peratures without the reaction. The furnace temperatures measured in the reactor with only Ar flow is shown in figures with dotted or dash-dot lines. As shown in the figures, the actual furnace temperatures were not uniform, such that the temperature went up as the position was higher due to the buoyancy. The furnace temperature difference between both ends of the monolith was about 10-17 K, depending on the set furnace temperature. The set furnace temperature denotes here the representative furnace temperature at the +15 mm position. ΔT is the temperature difference at the same position between the measured temperature in the reactor during the reaction and the furnace temperature in the reactor without the reaction.

1-1. CH₄ Combustion-CO₂ Reforming of CH₄ with x of 1

Figs. 2 and 3 show the temperature profiles in the case of the feed composition of CH₄ : O₂ : CO₂ : Ar being 20 : 5 : 10 : 65 ($x=1$) with down-flow and up-flow of the reactant gas.

Fig. 2 shows the temperature profiles of the monolith reactor with the down-flow of the gas. At a set furnace temperature of 573 K, actually no reaction occurred. This is because the ignition temperature of the CH₄ combustion over this catalyst is about 623-673 K [Kong, 2002; Kong et al., 2002].

At the set furnace temperatures of 673 and 773 K, ΔT 's at the inlet of the monolith were about +60 and +50 K, respectively. This indicates that complete combustion of CH₄ exclusively occurred near the inlet of the monolith. It was also noticed that the temperatures in the region above (before) the monolith, at least up to -15

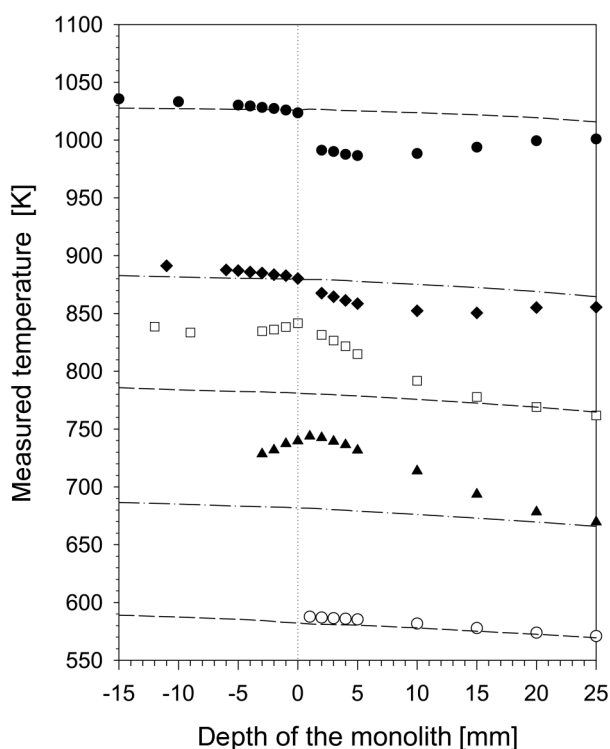


Fig. 2. Temperature profiles of the monolith reactor with the down-flow of the gas in CH₄ combustion-CO₂ reforming of CH₄ ($x=1$) for different furnace temperatures; ○: 573 K; ▲: 673 K; □: 773 K; ◆: 873 K; ◇: 973 K; ●: 1,023 K; ▽: 1,073 K; --- or -.-: temperature profile at each furnace temperature without reaction.

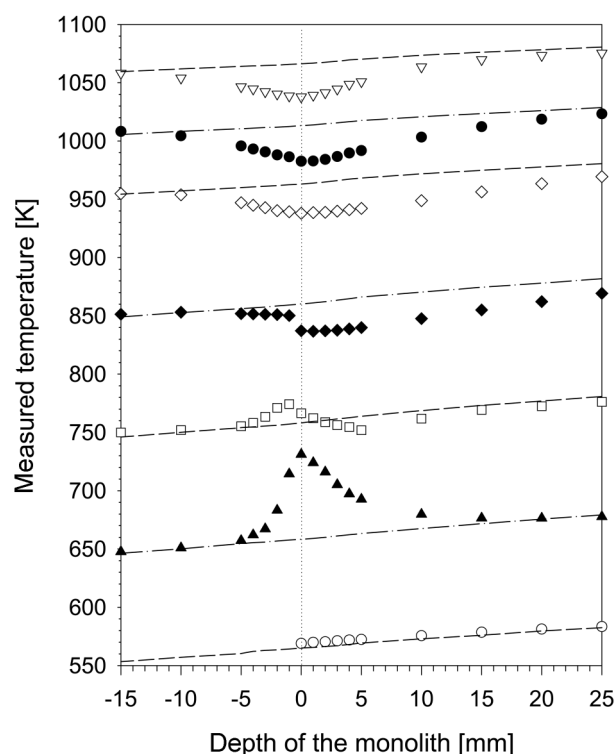


Fig. 3. Temperature profiles of the monolith reactor with the up-flow of the gas in CH₄ combustion-CO₂ reforming of CH₄ ($x=1$) for different furnace temperatures; ○: 573 K; ▲: 673 K; □: 773 K; ◆: 873 K; ◇: 973 K; ●: 1,023 K; ▽: 1,073 K; --- or -.-: temperature profile at each furnace temperature without reaction.

Table 1. Results of CH₄ combustion-CO₂ reforming of CH₄ (x=1 and 7) over (5)CeO₂-(10)Ni-(1)Pt/Al₂O₃ coated on a monolith

Set furnace temp. [K]			673	773	873	973	1023	1073
X=1	down-flow	CH ₄ conv.	12.7	24.5	48.7	77.5	88.4	93.6
		CO yield	0.1	10.7	39.1	73.9	85.2	92.7
		CO ₂ disch./in. ratio	1.00	1.25	1.17	0.80	0.21	0.09
	up-flow	CH ₄ conv.	13.3	22.3	54.3	74.3	90.0	97.0
		CO yield	0.8	9.0	48.0	71.2	92.0	97.8
		CO ₂ disch./in. ratio	1.24	1.17	1.18	0.35	0.04	0.01
X=7	down-flow	CH ₄ conv.	19.2	25.3	29.2	45.6	44.9	65.1
		CO yield	0.0	0.0	3.0	27.1	37.7	52.9
		CO ₂ disch./in. ratio	2.54	3.03	3.06	2.21	1.20	1.24
	up-flow	CH ₄ conv.	6.4	36.1	42.7	59.1	58.3	72.2
		CO yield	0.9	5.4	15.0	37.6	53.3	68.2
		CO ₂ disch./in. ratio	1.43	3.40	3.07	2.34	0.87	0.64

mm position, were significantly higher than the furnace temperature. This is because the gas heated by the combustion readily goes back by sudden expansion or goes up owing to buoyancy. As the gas went through into the monolith, ΔT was decreased. This is considered due to two major reasons. One is the heat loss through the reactor sidewall, and the other is the endothermic reaction of reforming. At the set furnace temperature of 673 K, the endothermic reforming reactions occurred little as shown by the results in Table 1. Therefore, the temperature decrease is certainly due to the heat loss. At the set furnace temperature of 773 K, the decreasing slope of the temperature to the downward position was steeper than that at 673 K. This indicates that a reforming reaction occurred somewhat more due to a higher temperature, as shown by the results in Table 1. At this temperature, the temperature decrease is caused by the above two reasons, with one being comparable to the other.

Above 873 K, it is evident that the endothermic reforming reaction predominately occurred even at the inlet of the monolith, probably due to even higher temperatures. The measured temperatures at the inlet of the monolith were almost the same as the furnace temperatures, but the measured temperatures right on the inside of the monolith were significantly lower than the furnace temperatures. The lowest measured temperatures were observed at +5 ~ +10 mm positions, ΔT 's being -20 ~ -40 K. Most of the reforming would have occurred before these points. It is certain that abrupt complete combustion did not occur, but a mildly exothermic reaction such as partial oxidation of methane might have occurred simultaneously with the reforming reaction, with the latter being dominant over the former. Consequently, the hot spot did not appear. The gradual temperature rise after +5 ~ +10 mm positions is thought due to a combination of diminishing extent of reforming reactions, sustenance of partial oxidation occurring, and heat supply from the reactor wall.

Fig. 3 shows the temperature profiles of the monolith with x of 1 with the up-flow of the gas. Again at the set furnace temperature of 573 K, no reaction occurred. At 673 K, most of the combustion occurred at the inlet of the monolith; therefore, the measured temperature became much higher than the furnace temperature (about +70 K). Although the heated gas passed through the monolith, the measured temperature became lower rapidly. But the reforming reaction occurred only to a very small extent, as seen in Table 1. The main reason for this lowering of the measured temperature is con-

sidered due to the radial heat loss through the reactor wall. Unlike the case of the down-flow of gas, the heat liberated by the combustion did not appear to transport well to the region below (in front of) the monolith. It affected only to the -5 mm position. This is because the heated gas naturally goes up owing to buoyancy, so the heat does not transfer well downward.

At the set furnace temperature of 773 K, ΔT at -1 mm position in front of the monolith was only +17 K. The measured temperature dropped and became lower than the furnace temperature after the +3 mm position in the monolith. Complete combustion might occur considerably at the inlet of the monolith. In this case the reforming reaction also occurred considerably from the inlet of the monolith, which will prevent abrupt ignition due to the counterbalancing effect of the endothermic reaction. This is contrasted with the case of the down-flow at the same furnace temperature where the hot spot appears. This observation suggests that the utilization of the heat by the *in-situ* exothermic reaction to the endothermic reaction is more effective with the up-flow operation than with the down-flow operation. At the set furnace temperatures higher than 873 K, the monolith temperature became significantly lower than the furnace temperature right from the inlet of the monolith owing to the reforming reaction. Complete combustion hardly occurred, but mild partial oxidation might have occurred simultaneously. Unlike the case of the down-flow of the gas, the temperature of the gas below the monolith was lower than the furnace temperature, down to about -10 mm position. This is again certainly due to the buoyancy, or denser cooler gas going downward.

There was not a significant difference in CH₄ conversion and CO yield between the cases of down-flow and up-flow, as shown in Table 1. With down-flow, the measured temperature near the inlet was higher but that in the rear part was relatively lower. With up-flow, the situation is vice versa. Therefore, this is considered to bring out little difference in the reaction results.

1-2. CH₄ Combustion-CO₂ Reforming of CH₄ with x of 7

Next, the temperature profiles of the monolith with x of 7 were examined. Here the compositions of CH₄ and O₂ were relatively higher than those with x of 1. The temperature profiles with down-flow and up-flow are shown in Figs. 4 and 5, respectively, and results of the reaction experiments are shown in Table 1. With down-flow, no reaction occurred at 573 K. Compared with the case of x of 1, the

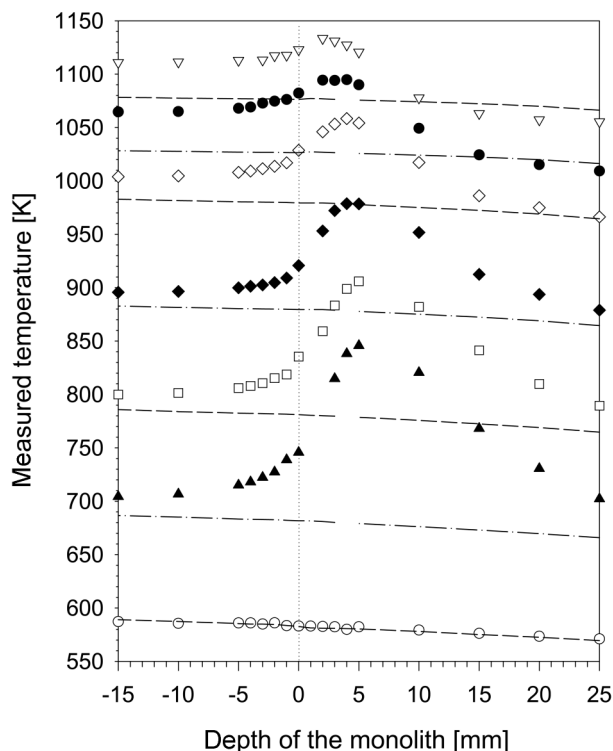


Fig. 4. Temperature profiles of the monolith reactor with the down-flow of the gas in CH₄ combustion-CO₂ reforming of CH₄ ($x=7$) for different furnace temperatures; ○: 573 K; ▲: 673 K; □: 773 K; ◆: 873 K; ◇: 973 K; ●: 1,023 K; ▽: 1,073 K; ---- or ---: temperature profile at each furnace temperature without reaction.

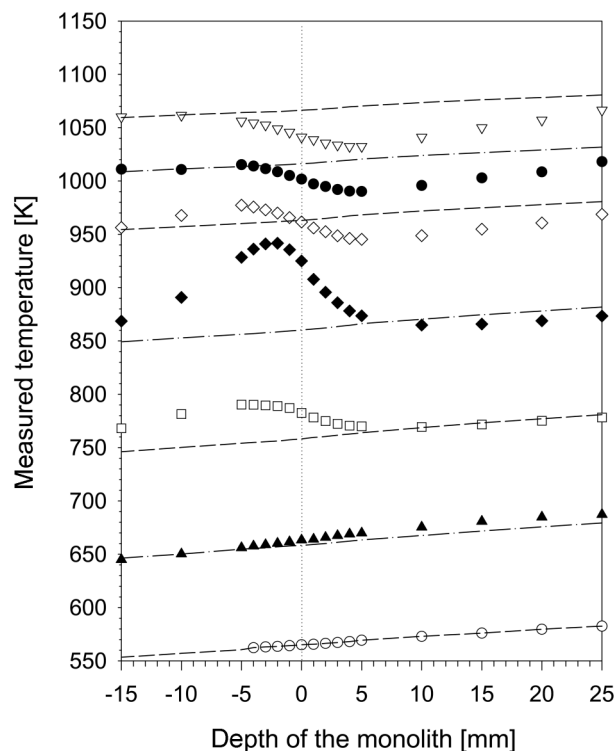


Fig. 5. Temperature profiles of the monolith reactor with the up-flow of the gas in CH₄ combustion-CO₂ reforming of CH₄ ($x=7$) for different furnace temperatures; ○: 573 K; ▲: 673 K; □: 773 K; ◆: 873 K; ◇: 973 K; ●: 1,023 K; ▽: 1,073 K; ---- or ---: temperature profile at each furnace temperature without reaction.

measured temperature rise was more pronounced in general. Above the set furnace temperature of 673 K, up to 1,073 K, the highest ΔT 's were observed at +2~+5 mm positions. This indicates that, unlike the case with x of 1, the combustion occurred predominantly from the 0 through +5 mm position. This is due to larger amount of CH₄ and O₂ fed. It was also observed that the temperature of the region above the monolith was quite higher than the furnace temperature. This is due to the buoyancy. As the furnace temperature became higher, the position of the highest measured temperature was moved from the +5 mm position toward the inlet of the monolith and the highest ΔT became smaller. This indicates that the reforming reactions occur to a greater extent with the temperature increase. In addition, the ignition phenomenon was observed up to as high as 1,073 K.

When comparing the case of x of 7 with that of x of 1 at 1,023 and 1,073 K, where the reforming reactions occurred to a great extent, the following results were obtained. The methane conversions for x of 7 were 45-65%, and these were lower by 25-30% than those for x of 1. The CO yields of 38-53% for x of 7 were lower by 30-35% than those for x of 1. This may be explained as follows: when x was 1, the reforming reactions occurred predominately from the inlet of the monolith. On the contrary, when x was 7, complete combustion and the reforming reactions might have occurred competitively from the inlet of the monolith through a good part deep inside (to +5~+10 mm), but because a higher amount of O₂ was supplied complete combustion occurred predominately. With the exhaustion

of the O₂, the reforming reaction could occur regularly. Accordingly, the effective length of the monolith that was used for the reforming reaction became relatively shorter. Moreover, as the production of H₂O was great, the steam reforming could prevail over the CO₂ reforming. As a result, CO₂ discharge/input ratios obtained at 1,023 and 1,073 were 1.20 and 1.14, respectively. This means that the large amount of CO₂ produced by combustion could not be removed effectively.

Fig. 5 shows the temperature profiles of the monolith for x of 7 with the up-flow of the gas. At a set furnace temperature of 573 K, the CH₄ combustion did not occur. At 673 K, abrupt ignition was not observed. But since the measured temperature in the monolith was somewhat higher than the furnace temperature, this indicates that some exothermic reactions occurred mildly throughout the monolith. At 773 K, ignition appeared to occur at the inlet. In addition, it appears that a flame was present at the region before the monolith, since the highest ΔT 's were observed at the -5~-2 mm position. This indicates that the flame caught at the inlet was easily and immediately propagated to a region somewhat before the monolith. At 873 K, it was observed that the measured temperature rapidly dropped and became lower than the furnace temperature at the rear part of the monolith. This indicates that the reforming reactions occurred to a large extent, when compared with the case of down-flow of the gas, and that the ignition occurred only at a narrow region of the inlet of the monolith. Above the furnace temperature of 973 K, ignition did not

occur. The reforming reactions did occur from the inlet of the monolith to a great extent, resulting in self-extinguishment of the flame, and the lowest temperature appeared at around the +5 mm position. This is contrasted with the case of x of 1 with the up-flow, where the lowest temperature appeared at around +2 mm position. ΔT 's were larger in this case. This is surely due to the large extent of the reforming reactions.

The results of the reaction experiments are also shown in Table 1. At 1,023 and 1,073 K, the CH_4 conversions were 58 and 72%, respectively. These were lower by 16–18% when compared with the case of x of 1, but higher by 7–13% compared with the case of down-flow with same x . The CO yields were 58 and 68%, respectively. These were lower by 20–24% when compared with the case of x of 1, but higher by about 15% compared with the case of down-flow with same x .

When comparing the case of up-flow with that of down-flow with x of 7, the most pronounced difference is that in the former a hot spot was not observed above 973 K, while in the latter a hot spot was observed up to 1,073 K. Higher values of CH_4 conversions and CO yields were another big difference. Even if abrupt ignition did not occur above 973 K with the up-flow of the gas, the O_2 was exhausted almost completely. In this case, it may be assumed that, rather than complete combustion, a mild exothermic reaction of partial oxidation of CH_4 ($\text{CH}_4/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$) could occur throughout the monolith. This suggestion may be supported strongly by the fact that nickel and platinum are also good catalysts for the partial oxidation in this temperature range [Jun et al., 2003, 2004a, b; Kim et al., 2003; Tomiainen et al., 1994]. In this situation, the steam reforming, which competes with the CO_2 reforming of CH_4 , is minimized since there is little production of H_2O . As a result, the CO_2 removal can become higher. When partial oxidation occurs predominantly over complete oxidation, the CH_4 conversion will become higher since the reaction rate of the partial oxidation is faster than that of the reforming reactions. With down-flow of the gas, on the contrary, the complete oxidation of CH_4 predominantly occurs first and then the steam and CO_2 reforming reactions follow with lowering of the temperature. Thus, this will result in decrease of the CH_4 conversion and the CO_2 removal.

2. C_2H_6 Combustion- CO_2 Reforming of C_2H_6

Ethane was fed together with O_2 , CH_4 , CO_2 and the diluent (with y of 0.3) so that heat liberated by the combustion of ethane could be utilized. The C_2H_6 combustion- CO_2 reforming of CH_4 was carried out with down-flow as well as up-flow of the reactant gas. The results of the reaction experiments are presented in Table 2.

The temperature profiles in the reactor with the down-flow are shown in Fig. 6. Abrupt ignition was observed from 673 K to 873 K.

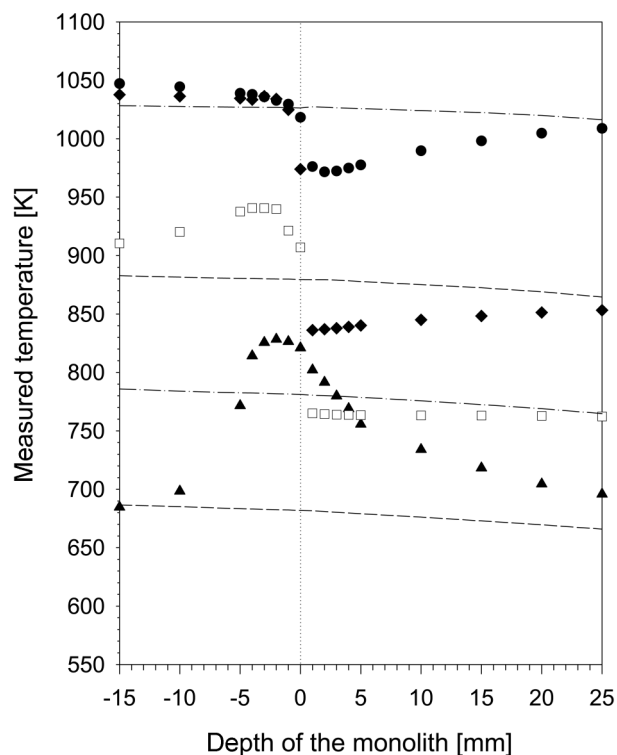


Fig. 6. Temperature profiles of the monolith reactor with the down-flow of the gas in C_2H_6 combustion- CO_2 reforming of CH_4 ($y=0.3$) over (5) CeO_2 -(10) Ni -(1) $\text{Pt}/\text{Al}_2\text{O}_3$ coated on a monolith for different furnace temperatures; $\blacktriangle$: 673 K; $\square$: 773 K; $\blacklozenge$: 873 K; $\bullet$: 1,023 K; — or - - - : temperature profile at each furnace temperature without reaction.

This is apparently due to the combustion of ethane. The highest ΔT 's were observed at around -2 mm position: they were about +150 K, +170 and +110 K, respectively. This means that the flame propagates upward and almost all the ethane is burnt in the gas phase.

At a set furnace temperature of 673 K, the reforming reaction occurred to a minute extent (Table 2). The temperature lowering in the bed of the monolith is again considered due to heat loss through the side reactor wall. At the set furnace temperatures of 773 K and 873 K, sudden temperature drops were observed at the inlet of the bed. Due to the high temperature brought by the combustion, the reforming reactions could start with the assistance of the catalyst in the monolith. Consequently, the temperature dropped abruptly. The ΔT 's at +1 mm position at 773 and 873 K were measured to be about -20 and -45 K. After the +1~+2 mm positions in the monolith, the measured temperature rose gradually. This is also considered

Table 2. Results of C_2H_6 combustion- CO_2 reforming of CH_4 ($y=0.3$) over (5) CeO_2 -(10) Ni -(1) $\text{Pt}/\text{Al}_2\text{O}_3$ coated on a monolith

Set furnace temp. [K]	Down-flow			Up-flow		
	C_2H_6 conv.	CH_4 conv.	CO yield	C_2H_6 conv.	CH_4 conv.	CO yield
573	66.2	11.8	1.2	0.0	0.0	0.0
673	77.0	10.8	3.3	56.4	10.7	1.1
773	89.7	27.7	12.0	67.6	8.3	2.8
873	100.0	39.4	37.0	89.3	24.6	23.9
1,023	100.0	80.9	83.8	98.2	67.5	69.6

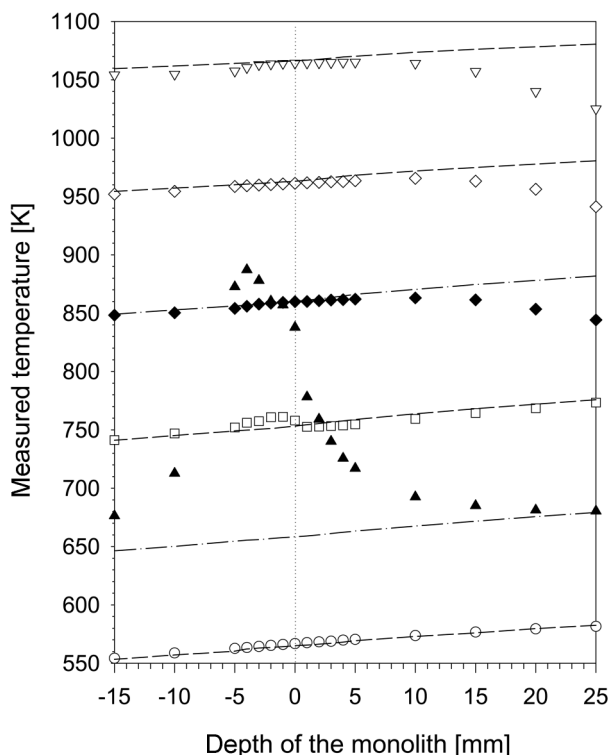


Fig. 7. Temperature profiles of the monolith reactor with the up-flow of the gas in C₂H₆ combustion-CO₂ reforming of CH₄ (y=0.3) over (5)CeO₂-(10)Ni-(1)Pt/Al₂O₃ coated on a monolith for different furnace temperatures; ○: 573 K; ▲: 673 K; □: 773 K; ◆: 873 K; ◇: 973 K; ▽: 1,073 K; — or ---: temperature profile at each furnace temperature without reaction.

due to the heat supply from the outside. This sort of temperature profile suggests that the reforming reactions occur in a narrow region near the monolith inlet.

At a set furnace temperature of 1,023 K, a hot spot was not observed and the reforming reactions occurred predominately from the inlet of the monolith. ΔT 's were -8 K at 0 and -50 K at the $+1$ mm position. The reforming reactions are considered to occur throughout the catalyst bed because the temperature was high. Due to the heat supply from the outside, the measured temperature in the monolith ascended gradually and ΔT at $+25$ mm position was -7 K. It was considered that a mild exothermic reaction occurred to some extent at this temperature because ΔT before the monolith was positive. This reaction may be oxidative dehydrogenation of the ethane ($C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O$), since this reaction can occur in the gas phase reaction without catalyst and also occur owing to the catalytic action of the stainless-steel sheath of the thermocouple, as already reported in an earlier study [Jun, 1998].

Fig. 7 shows the temperature profiles with the up-flow of the gas with the same composition. At 673 K, likewise to the case of down-flow, C₂H₆ combustion began at the inlet of the monolith and then the flame burst out and propagated, as ΔT at 0 mm position was $+180$ K, and the highest ΔT , as high as 230 K, was observed at -4 mm position. At 773 K, a hot spot was not observed. When the gas passed through the monolith, the measured temperature was almost the same as the furnace temperature. This may be explained as that

the exothermic complete combustion or the partial oxidation and the endothermic reforming reactions occur simultaneously and that the heats of the reactions appear to keep a balance between them. Actually, it was observed that when the reaction was just started, the catalyst bed temperature rose abruptly by the ignition. However, after a while, ΔT became smaller and smaller and the reactor reached steady state. The initial high temperature would have induced the endothermic reforming reactions, resulting in self-extinguishment of the flame. ΔT at -2 mm was $+9$ K, and this suggests that a mild exothermic reaction (for instance, the oxidative dehydrogenation of the ethane) could occur to some extent.

At the furnace temperatures of 873, 973 and 1,073 K, the temperature profiles were similar to each other. Near the inlet of the monolith, again the exothermic and endothermic reactions appeared to occur simultaneously and to make the heats balanced. In addition, it may be considered that the exothermic reaction in this region is milder and progresses more slowly. For instance, as ethane is more reactive than methane, partial oxidation of ethane (e.g., $C_2H_6 + 5/2O_2 \rightarrow 2CO + 3H_2O$ or $C_2H_6 + O_2 \rightarrow 2CO + 3H_2$) may occur first, and then the steam or CO₂ reforming of the methane may follow. As the reactant gas passed through the monolith, the endothermic reforming reaction became gradually prevalent and thus the measured temperature at $+25$ mm position became considerably lower. ΔT 's at $+25$ mm position were -37 K at the set furnace temperature of 873 K, -40 K at 973 K and -56 K at 1,073 K. This shows that the endothermic reactions occur more and more as the reaction temperature becomes higher.

When comparing the conversion and the yield, the results obtained with the down-flow operation were higher than those with the up-flow. This is considered due to that with the down-flow the ethane being burnt abruptly and the catalyst bed temperature becoming considerably high, so that the reforming reaction could occur to a greater extent. It is considered that most of the reforming reactions occurred near the inlet of the monolith. With the up-flow, however, the ethane was not burnt abruptly and so the temperature near the inlet of the catalyst was relatively low. The partial oxidation of the ethane might progress slowly and compete with the reforming of methane. At the rear part of the monolith, the reforming of methane could occur regularly, but the measured temperature became much lower and thus the reaction rate became much slower. Consequently, the overall results of the CH₄ conversion and CO yield became lower.

CONCLUSIONS

The temperature profiles in the monolith reactor were measured with down-flow as well as up-flow of the reactant gas. The following results were obtained:

Regardless of the flow direction, a hot spot was observed at low furnace temperatures (673–873 K) because the combustion occurred abruptly near the inlet of the monolith, to bring out the flame. As the furnace temperature increased, the hot spot tended to disappear. This is due to natural extinguishment of the flame, because the endothermic reforming reaction occurs more and more with the increase of the temperature. As the reforming reactions occurred to a greater extent, the catalyst bed temperature became considerably lower than the furnace temperature.

With the down-flow of the gas the possibility of inflammation at the inlet of the monolith was higher than with the up-flow of the gas. When ethane that has a higher reactivity than methane or a higher amount of O_2 was supplied, the hot spot appeared up to about 1,000 K. With the up-flow, the hot spot did not appear above 973 K. This is because a gas heated by an exothermic reaction readily goes up into the monolith and thus promotes the endothermic reforming reaction, resulting in the flame extinguishing itself. When a hot spot appears at a region before the monolith, the heat loss through the reactor side is considered great; thus the released heat from the combustion would not effectively be used for the endothermic CH_4 reforming.

In the CH_4 combustion- CO_2 reforming of CH_4 , when a hot spot appears, H_2O and CO_2 are produced with the exhaustion of the O_2 . Accordingly, the steam reforming and the CO_2 reforming occur competitively in the rear part of the monolith. As the reaction rate of the steam reforming reaction is faster than that of the CO_2 reforming reaction, the efficiency of CO_2 removal was reduced. In case that the hot spot does not appear, it is considered that the partial oxidation of methane may occur predominantly over the complete oxidation. As the reaction rate of partial oxidation is faster than that of the reforming reaction, the CH_4 conversion can become higher. Moreover, as the production of H_2O and CO_2 is minimized, the CO_2 can be removed more efficiently. Therefore, in order to obtain better performance in CO_2 removal, it is necessary for the reactor to be operated under the conditions that prevent the hot spot, such as up-flow, high temperature and low x . When x is high, feeding of CH_4 and O_2 distributed along the reactor side may be more effective than co-feeding all the gases at once.

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