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Transient response of catalyst bed temperature in the pulsed reaction of partial oxidation of methane to synthesis gas over supported group VIII metal catalysts

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Abstract

Mechanisms of partial oxidation of methane to synthesis gas were studied using a pulsed reaction technique and temperature jump measurement. Catalyst bed temperatures were directly measured by introducing 1 and 3 ml pulses of a mixture of CH_4 and O_2 (2/1). With Ir, Pt and Ni/TiO_2 catalysts, a sudden temperature increase at the front edge of the catalyst bed was observed upon introduction of the pulse. The synthesis gas production basically proceeded via two-step paths consisting of highly exothermic complete methane oxidation to give H_2O and CO_2, followed by the endothermic reforming of methane with H_2O and CO_2. In contrast, with the Rh and Pd/TiO_2 catalysts, the temperature at the front edge of the catalyst bed decreased upon introduction of the CH_4/O_2 (2/1) pulse and a small increase in the temperature at the rear end was observed. Initially, the endothermic decomposition of CH_4 to H_2 and deposited carbon or CH_x probably took place at the front edge of the catalyst bed, after which the deposited carbon or generated CH_x species would be oxidized into CO_x. When the Ru/TiO_2 catalyst was used, a temperature increase at the front edge of the catalyst bed was observed upon introduction of the 3 ml pulse of CH_4/O_2. In contrast, the temperature drop at the front edge of the catalyst bed was observed for a 1 ml pulse of CH_4/O_2. These results seemed to exhibit two possibilities for a synthesis gas formation route over the Ru/TiO_2 catalyst. The reaction pathway of the partial oxidation of methane with group VIII metal-loaded catalysts depended strongly upon the metal species and reaction conditions.

Keywords: Partial oxidation; Iridium; Platinum; Palladium; Rhodium; Ruthenium; Nickel; Titania; Pulsed reaction; Methane decomposition

1. Introduction

Synthesis gas production from methane is indispensable for the chemical utilization of natural gas, such as in dimethyl ether, methanol and Fischer–Tropsch syntheses. The partial oxidation of methane has attracted much attention, the reaction is as follows:

$$\text{Partial oxidation}: \quad CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \quad \Delta H^0_{298} = -36\,\text{kJ/mol} \qquad (1)$$

Two reaction pathways have been proposed to account for the catalytic conversion of methane with oxygen to synthesis gas. Methane combustion, followed by steam and CO_2 reformings are commonly accepted

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mechanisms which are as follows:

$$\text{Combustion}: \quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H^0_{298} = -801\,\text{kJ/mol} \tag{2}$$

$$\text{Steam reforming}: \quad CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H^0_{298} = +206\,\text{kJ/mol} \tag{3}$$

$$CO_2\ \text{reforming}: \quad CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H^0_{298} = +247\,\text{kJ/mol} \tag{4}$$

Nakamura et al. [1] investigated the same reaction over a SiO_2-supported rhodium catalyst and concluded that the primary products of CO_2 and H_2O found at 600–700 K were further converted into CO and H_2 through the reactions of CH_4 with CO_2 and H_2O at an elevated temperature. We have previously reported that a Ir/TiO_2 catalyst has promoted the reaction sequence of the total oxidation of methane to CO_2 and H_2O, as well as the reforming reactions to synthesis gas. The CH_4 conversion, as well as the CO and H_2 selectivities, decreased with increasing space velocity, but the CO_2 selectivity increased over the Ir/TiO_2 catalyst [2,3].

The other pathway is the direct course. Hickman and coworkers [4–7] investigated alumina monolith-supported rhodium and platinum catalysts for the partial oxidation of methane under an extremely short residence time between 10^{-4} and 10^{-2} s. A very high selectivity to synthesis gas (>90%) was observed, indicating the direct pathway of CH_4 to CO and H_2. Boucouvalas et al. [8,9] reported that an Ru/TiO_2 catalyst promotes the direct formation of synthesis gas and that high CO and H_2 selectivities were obtained over Ru/TiO_2 catalyst at methane conversions approaching zero.

Prettre et al. [10] reported that the temperature at the front of the catalyst bed using a supported nickel catalyst was found to be much higher than the furnace temperature and that a temperature drop occurred in the inner part of the catalyst bed. Such phenomena have also been observed by other researchers [11,12].

We have performed detailed analyses of the reaction pathway of the partial oxidation of methane to synthesis gas over Ir- and Rh-loaded catalysts using a transient response of the catalyst bed temperature in a pulsed reaction. The temperature jump measurement technique was effective in evaluating an exothermic or endothermic reaction path methodology and the validity of this measurement for the test of exothermic or endothermic reactions has been confirmed [13]. In this study, the measurement of the temperature jump was extended to examine the reaction pathway of the partial oxidation of methane to synthesis gas using various TiO_2-supported group VIII metal catalysts.

2. Experimental

TiO_2 (Japan Aerosil, surface area: 50 m^2/g) was used as the support. The supported group VIII metal catalysts containing 5 wt.% metal were prepared by the impregnation method. Supported catalysts were calcined at 873 K for 5 h in air prior to the reaction.

Transient response measurements of the catalyst bed temperature in the pulsed reactions were carried out using a fixed bed quartz reactor (i.d. 4 × 200 mm). Two thin wall-sheathed K-type thermocouples (outer diameter 0.6 mm) were placed at the front edge and the rear end of the catalyst bed and 100 mg of the catalyst was charged. A pulse of CH_4 and O_2 (2/1) mixed gas was introduced with a six port gas sampling valve equipped with measuring tubes, under a stream of Ar carrier gas. The reaction system has been described elsewhere in detail [13]. Before the reaction, the catalysts were reduced with H_2 for 1 h at 873 K. Analyses of the gases during the pulsed reactions were made using an on-line quadrupole mass spectrometer (HAL201, Hiden Analytical). The mass spectrometer scanned the parent peaks of the five compounds, H_2, CH_4, CO, O_2 and CO_2, within 1 s and repeated scans were collected in a personal computer. Measured intensities were corrected for the relative sensitivities of the respective ions. All the pulsed reactions were repeated more than two runs and reproducible results were obtained.

3. Results and discussion

3.1. Effect of TiO_2-supported group VIII metal catalysts on the partial oxidation of methane

Table 1 shows the product distribution of the partial oxidation of TiO_2-supported group VIII metal catalysts [2]. Supported catalysts were calcined at 873 K

Table 1
Activity of various TiO_2-supported catalysts for partial oxidation at 873 K [2][a]

Catalyst	CH_4 conversion (%)	CO selectivity (%)	CO_2 selectivity (%)	H_2 selectivity (%)	H_2/CO ratio
Rh/TiO_2	26.5	81.6	18.4	87.3	2.1
Ir/TiO_2	25.7	81.8	18.2	83.1	2.0
Ru/TiO_2	24.0	79.0	21.0	80.5	2.0
Pd/TiO_2	23.9	74.0	26.0	82.8	2.2
Pt/TiO_2	11.5	30.2	69.8	39.9	2.6
Ni/TiO_2	2.4	22.0	78.0	2.9	0.3
TiO_2	1.2	18.6	81.4	4.0	0.4

[a] Catalyst, 0.060 g; metal loading level = 5.0 wt.%; flow rate, 30.0 ml/min ($CH_4/O_2 = 5.0$); space velocity = 30 000 h^{-1} ml g-cat^{-1}.

in air prior to the reaction thus, oxidic forms of transition metals were used. The conversion of methane was affected by the metal species; their order of activity was Rh $\geqq$ Ir > Ru $\geqq$ Pd > Pt $\gg$ Ni. At 873 K, selectivities to CO and H_2 were the highest with the Rh, Ru and Ir/TiO_2 catalysts with a H_2 to CO ratio of 2.0–2.1 as expected from the stoichiometric equation (reaction (1)). Excess H_2 may be a result of the water-gas shift reaction or decomposition of CH_4 over Rh and Pd/TiO_2 catalysts. Pt and Ni/TiO_2 catalysts afforded higher CO_2 selectivity than that of Rh or Ir/TiO_2 catalysts. This seems to indicate that complete oxidation of CH_4 (reaction (2)) occurred mainly over the Pt/TiO_2 catalyst. The Ni/TiO_2 catalyst did not produce CO and H_2 in the temperature range 673–873 K and only complete oxidation of CH_4 occurred with very low activity. Metallic nickel was thought to be the active species in the partial oxidation of methane [11,14]. Nickel oxide loaded on TiO_2 seemed not to be reduced by CH_4, CO and H_2 below 873 K in the presence of O_2; consequently, Ni/TiO_2 could not be an effective catalyst for the partial oxidation of methane.

3.2. Decomposition of methane over TiO_2-supported group VIII metal catalysts

Figs. 1 and 2 show the transient response of H_2 production when the flowing gas was switched from Ar to CH_4 at 873 K (reaction (5)) over TiO_2-supported group VIII metal catalysts. H_2 was the only gaseous species observed (no higher hydrocarbons).

$$CH_4 \rightleftarrows C + 2H_2, \quad \Delta H^0_{298} = +75\,\text{kJ/mol} \qquad (5)$$

When CH_4 was supplied to Ir, Ru and Pt/TiO_2 catalysts, small H_2 responses appeared instantaneously

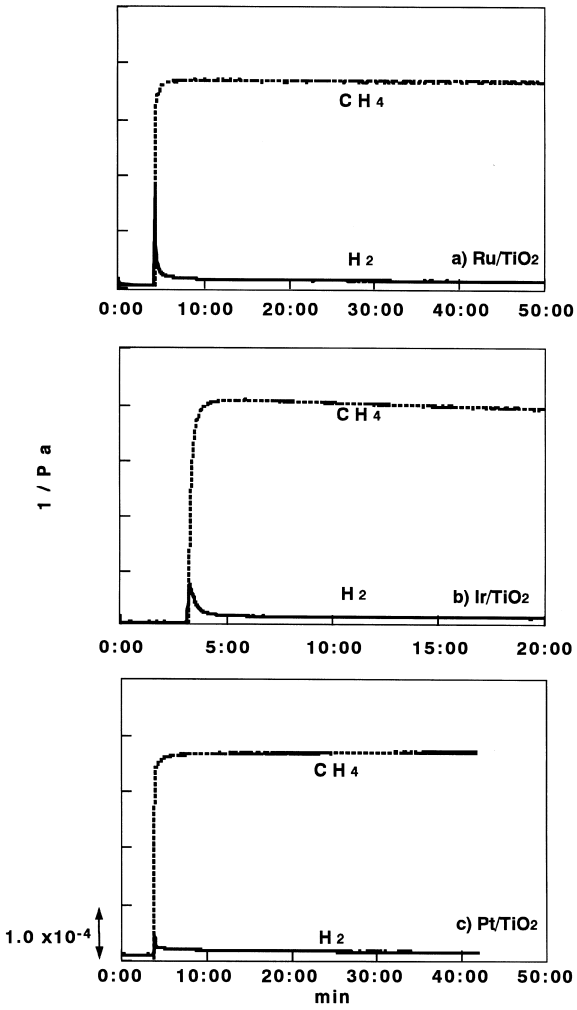

Fig. 1. Decomposition of CH_4 over Ru, Ir and Pt(5 wt.%)/TiO_2. Reaction conditions — temperature: 873 K, catalyst: 100 mg, CH_4 flow rate = 10 ml/min.

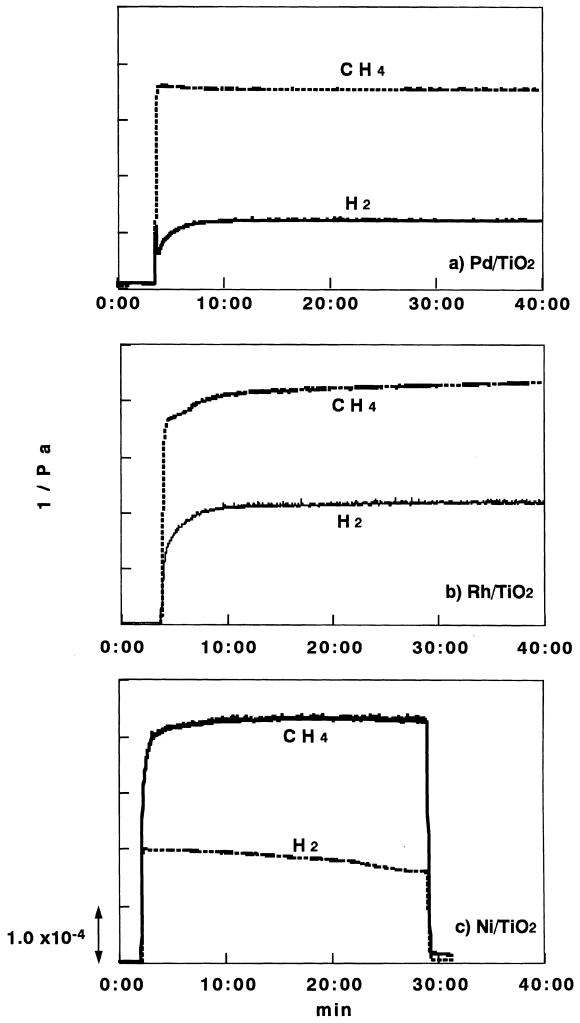

Fig. 2. Decomposition of CH_4 over Pd, Rh and Ni(5 wt.%)/TiO_2. Reaction conditions — temperature: 873 K, catalyst: 100 mg, CH_4 flow rate = 10 ml/min.

and then decreased to a low level. In contrast, methane decomposition continued to produce H_2 over Rh, Pd and Ni/TiO_2 catalysts for more than 40 min except for Ni/TiO_2. These results indicated that Rh, Pd and Ni/TiO_2 exhibited a much higher activity toward the decomposition of CH_4 than did Ir, Ru and Pt/TiO_2 catalysts.

Verykios and coworkers [15] reported the results of methane decomposition over Rh(0.5 wt.%)/Al_2O_3 catalyst at 923 K. They concluded that after 600 s on stream the rate of H_2 production decreased to about one-seventh of its initial rate. In our previous study, when CH_4 was supplied to Rh(5.0 wt.%)/Al_2O_3 catalyst initially showed a high activity towards decomposition of CH_4. However, the H_2 concentration gradually decreased with increasing time-on-stream and H_2 production was not detected after 4800 s. In contrast, methane decomposition continued to produce H_2 over the Rh/TiO_2 catalyst for 2400 s [13].

Table 2
Temperature programmed reduction with H_2 over TiO_2-supported group VIII metal catalyst[a]

Catalyst	Reduction temperature (K)	
	Initial	Maximum reduction rate
Pd/TiO_2	415.7	415.7
Rh/TiO_2	455.9	455.9
Ru/TiO_2	541.6	552.3
Pt/TiO_2	495.6	558.5
Ir/TiO_2	573.0	666.3
Ni/TiO_2	473.0	860.0

[a] Catalyst, 100 mg; heating rate, 20 K/min; flow rate, H_2 = 10 ml/min.

Table 2 and Fig. 3 show the results of temperature programmed reduction with H_2 over TiO_2-supported group VIII metal catalysts. Only H_2O was observed as a product. The maximum reduction temperatures increased in the following order in terms of elements: Pd < Rh < Ru < Pt < Ir < Ni. This order is consistent with the activity order of CH_4 decomposition. Pd and Rh/TiO_2 catalysts started to be reduced at temperatures as low as 423–453 K. In addition, maximum reduction temperatures of Pd and Rh/TiO_2 catalysts were lower than those of other metal-loaded catalysts. Pd and Rh/TiO_2 catalysts were easily reduced to metallic species and had a high CH_4 decomposition activity at 873 K.

The Ni/TiO_2 catalyst also exhibited high CH_4 decomposition. It was partly reduced at low temperatures; however, a high temperature of about 873 K was needed to reduce it completely. On the other hand, the Pt and Ir/TiO_2 catalysts which showed low activity for the CH_4 decomposition were reduced at higher temperatures than those of the Rh and Pd/TiO_2 catalysts. The Pt loaded catalyst did not show distinct reduction peaks. The reason for this seems to be that the Pt-loaded TiO_2 catalyst was not fully oxidized during oxidation at 873 K.

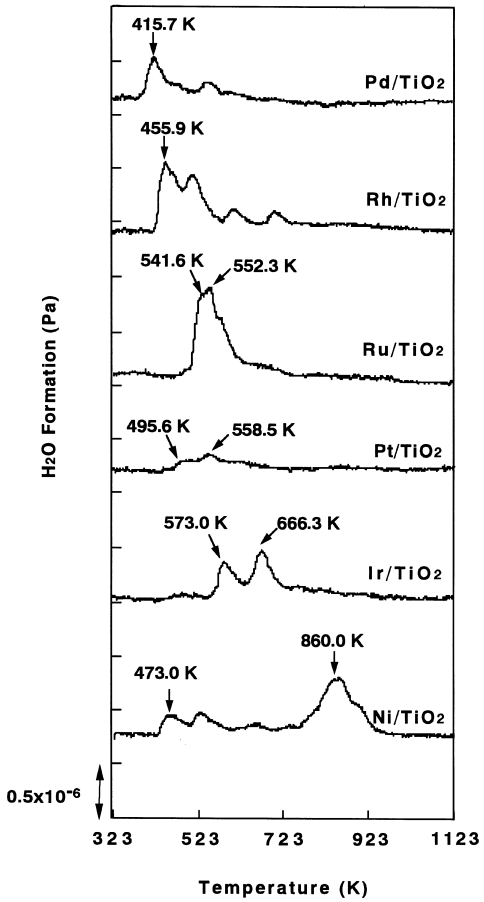

Fig. 3. Temperature programmed reaction with H_2 over TiO_2-supported catalysts. Reaction conditions — catalyst: 100 mg, metal loading level = 5 wt.%, heating rate: 20 K/min, flow rate: H_2 = 10 ml/min.

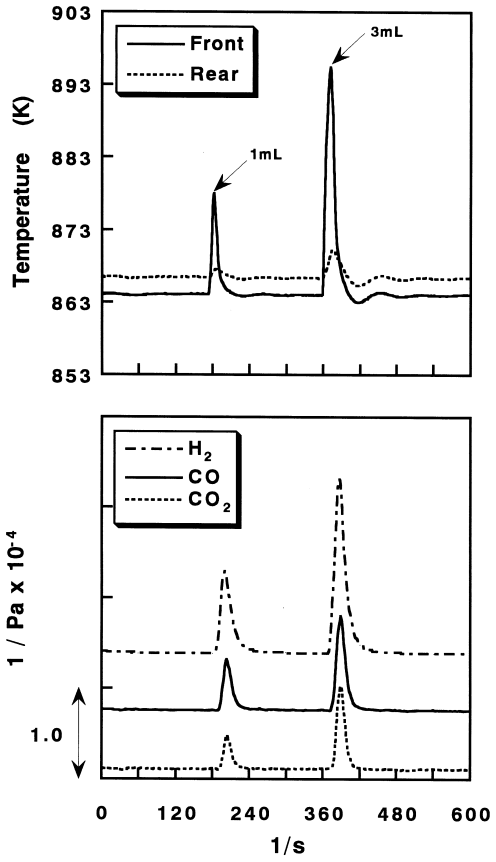

Fig. 4. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Ir(5 wt.%)/TiO_2 catalyst. Reaction conditions — Ar carrier = 10 ml/min, mixed gas: CH_4:O_2 = 2:1, 1 or 3 ml, furnace temperature: 873 K.

3.3. Transient response of catalyst bed temperature in the pulsed reaction of partial oxidation of methane

3.3.1. Ir, Pt and Ni/TiO_2 catalysts

Figs. 4–6 show the transient temperature responses of TiO_2-supported Ir, Pt and Ni catalysts against a pulsed injection of CH_4/O_2. The catalysts were reduced by H_2 flow for 1 h at 873 K. When the Ir, Pt and Ni/TiO_2 catalysts were used, a sudden large temperature rise at the front edge of the catalyst bed was observed upon introduction of the pulse, but the temperature of the rear end of the catalyst bed was only slightly increased. Especially, the Pt/TiO_2 catalyst which showed high CO_2 selectivity (Table 1) emerged a larger temperature rise than that of Ir and Ni/TiO_2 catalysts and a large amount of CO_2 was produced when a 3 ml of pulse was injected, indicating that a large amount of heat was generated at the front edge of the catalyst bed. The effluent of the pulsed reaction exhibited the formation of CO and H_2. The slight temperature increase of the rear edge of the catalyst bed on the Ir, Pt and Ni/TiO_2 catalysts might be ascribed to the heat conduction from the front and middle part of the catalyst bed.

Synthesis gas formation apparently proceeded via two pathways over the TiO_2-supported group VIII metal catalysts. One reaction pathway would be the two-step reactions, the reaction sequence of total

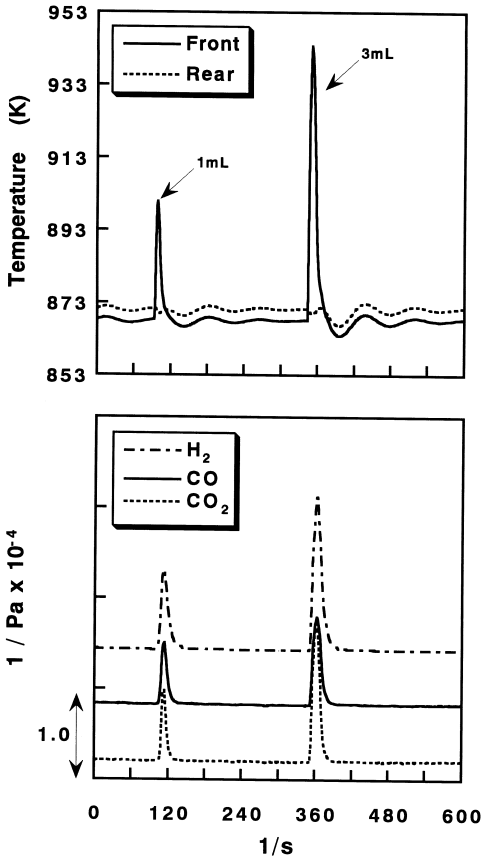

Fig. 5. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Pt(5 wt.%)/TiO_2 catalyst. Reaction conditions — Ar carrier = 10 ml/min, mixed gas: CH_4:O_2 = 2:1, 1 or 3 ml, furnace temperature: 873 K.

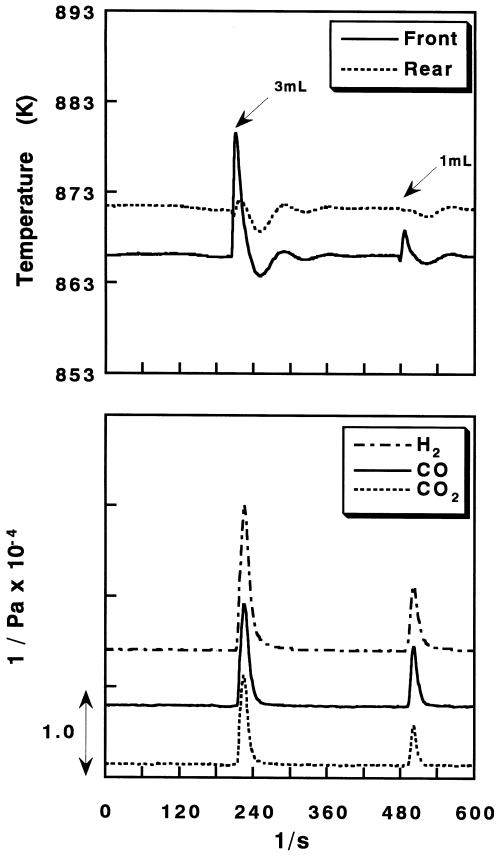

Fig. 6. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Ni(5 wt.%)/TiO_2 catalyst. Reaction conditions — Ar carrier = 10 ml/min, mixed gas: CH_4:O_2 = 2:1, 1 or 3 ml, furnace temperature: 873 K.

oxidation of methane to CO_2 and H_2O (reaction (3)) and reforming reactions to synthesis gas (reactions (3) and (4)) are involved. Another pathway might be CH_4 decomposition to H_2 and CH_x, following CH_x oxidation to CO_x. It is possible to induce both reaction pathways over TiO_2-supported group VIII metal catalysts.

In the high temperature range 1200–1400 K, Hickman and coworkers [4–7] investigated alumina monolith-supported rhodium and platinum catalysts for the partial oxidation of methane, under an extremely short residence time between 10^{-4} and 10^{-2} s. A very high selectivity to synthesis gas (>90%) was observed, indicating the direct pathway of CH_4 to CO and H_2. However, it is difficult to investigate reaction pathways using the thermodynamic equilibrium composition of product gases at high temperatures [14]. Therefore, we conducted detailed analyses of the reaction pathway of the partial oxidation of methane to synthesis gas using the transient response of the catalyst bed temperature to a pulsed reaction at a moderate temperature of 873 K.

The reaction pathway of synthesis gas production over the Ir, Pt and Ni/TiO_2 catalysts seemed to proceed mainly via the two-step reactions that the Ir, Pt and Ni/TiO_2 catalysts might have promoted the reaction sequence of total oxidation of methane to CO_2 and H_2O (reaction (2)), followed by reforming reactions to synthesis gas (reactions (3) and (4)). The Pt

and Ni/TiO_2 catalysts, however, would have shown low levels of reforming reactions to synthesis gas (reactions (3) and (4)) at 873 K. Lower activity of the Pt/TiO_2 catalyst for CO_2 and H_2O reforming was supported by results that the large temperature increases and higher CO_2 concentration were observed under steady flow than those of the Ir/TiO_2 catalyst. The NiO/TiO_2 catalyst exhibited very low activity for the partial oxidation under steady flow. However, in the pulsed reaction over hydrogen reduced Ni/TiO_2 catalyst, conversion of CH_4 to H_2 and CO was higher than Pt/TiO_2 catalyst, consequently, the temperature at the front edge of the Ni/TiO_2 catalyst bed was smaller than that of the Pt/TiO_2 catalyst.

If the heat loss from the catalyst bed and thermocouples were nil, the estimated temperature increase during complete oxidation would be ca. 473 K for the 3 ml pulse. In our apparatus, heat loss could not be eliminated. The observed temperature rise was about 30–70 K. Endothermic CO_2 and H_2O reforming reactions proceeded to induce not only heat loss from the reactor wall, but also to slow the rise in the temperature of the catalyst bed. If a direct partial oxidation reaction (reaction (1)) proceeded, due to the small degree of heat generation such a large rise in temperature could not be observed. Thus, when the Ir, Pt and Ni/TiO_2 catalysts were used, the temperature increase in the front edge of the catalyst bed could safely be ascribed to the complete oxidation of methane. In addition, Ir and Pt/TiO_2 catalysts induced low CH_4 decomposition to H_2 and CH_x (Fig. 1). Therefore, it would be difficult to produce synthesis gas using the formation route of CH_4 decomposition to H_2 and CH_x, following CH_x oxidation to CO_x.

In regard to the Ni/TiO_2 catalyst, it certainly had a high activity for decomposition of CH_4 in the absence of oxygen. In the presence of oxygen, however, NiO would be in a more stable state than would be Ni metal in the presence of oxygen below 873 K. Table 2 also shows the difficulty of reducing NiO to Ni metal at low temperatures. Ni(5 wt.%)/TiO_2 samples (both fresh and used) showed diffraction patterns ascribed to $NiTiO_3$ species as revealed by XRD [16]. There findings indicate that Ni oxide was not reduced to a metallic species. Reduced Ni/Al_2O_3 is an active catalyst and is commonly used in the partial oxidation of methane to synthesis gas, where metallic Ni has been regarded as the active component. However,

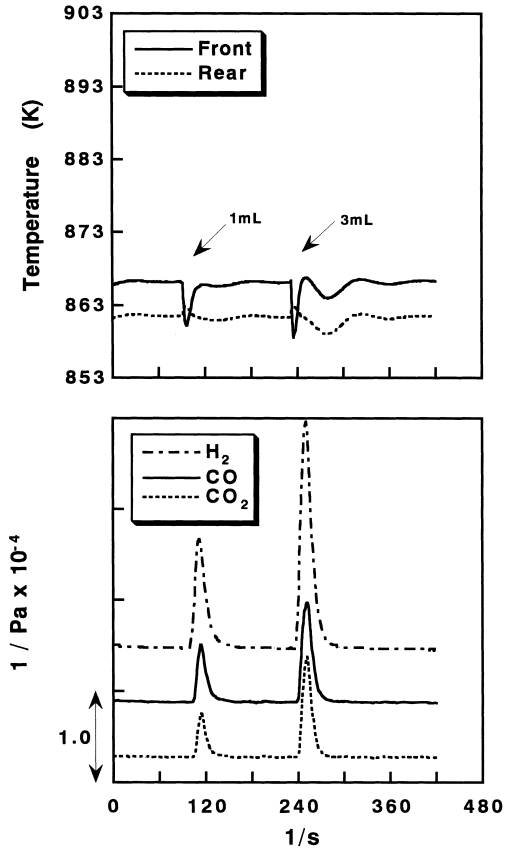

Fig. 7. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Rh(5 wt.%)/TiO_2 catalyst. Reaction conditions — Ar carrier = 10 ml/min, mixed gas: CH_4:O_2 = 2:1, 1 or 3 ml, furnace temperature: 873 K.

the inactive $NiAl_2O_4$ phase was often formed during calcination in air. Complete oxidation of methane to CO_2 and H_2O occurs at a low temperature over the oxidized NiO/Al_2O_3 or $NiAl_2O_4$ catalysts, but synthesis gas was produced only by a reduced Ni/Al_2O_3 catalyst at temperatures above 1023 K [11].

3.3.2. Rh, Pd and Ru/TiO_2 catalysts

Figs. 7 and 8 show the transient response temperature behavior of TiO_2-supported Rh and Pd catalysts induced by a pulsed injection of CH_4/O_2. The catalysts were reduced by H_2 flow for 1 h at 873 K before use. When the Rh and Pd/TiO_2 catalysts were used, in contrast to the above cases the temperature at the front edge decreased upon introduction of the CH_4/O_2

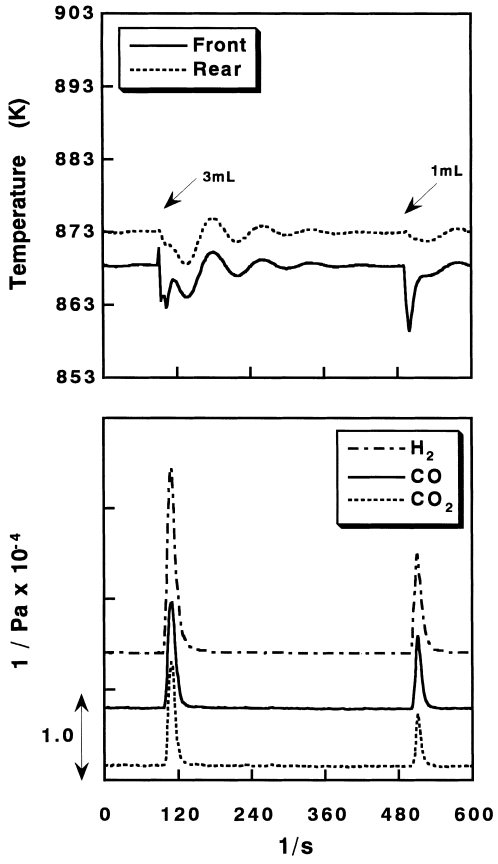

Fig. 8. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Pd(5 wt.%)/TiO_2 catalyst. Reaction conditions — Ar carrier = 10 ml/min, mixed gas: CH_4:O_2 = 2:1, 1 or 3 ml, furnace temperature: 873 K.

pulse and an increase in the temperature at the rear end was observed. It is surprising that the temperature drop at the front edge of the catalyst bed was observed for the Rh and Pd/TiO_2 catalysts, even when methane and oxygen were introduced in a ratio of 2/1. Rh and Pd/TiO_2 catalysts afforded high H_2 selectivities (Table 1) and large amounts of H_2 were also produced in the 3 ml pulsed reaction.

In the Pd/TiO_2 catalyst, initial temperature drop at the front edge of the catalyst bed was observed followed by the emergence of oscillatory phenomenon. This phenomenon would probably be similar to the oscillatory behavior seen over the Pt and Pd/Al_2O_3 catalysts on CO oxidation [17,18].

When the Ru/TiO_2 catalyst was used, a sudden rise in temperature at the front edge of the catalyst bed was observed upon introduction of the 3 ml pulse of CH_4 and O_2. However, a temperature drop at the front edge of the catalyst bed was observed for a 1 ml pulse of CH_4 and O_2 mixture.

The reaction pathway toward synthesis gas production over the Rh and Pd/TiO_2 catalysts seemed to mainly proceed via CH_4 decomposition to H_2 and CO_x, following CH_x oxidation to CO_x. In the steady flow, the Rh/TiO_2 catalyst maintained high H_2 selectivities even at high space velocities [13]. The Rh and Pd/TiO_2 catalysts had a high activity of methane decomposition (Fig. 2). Under high space velocity, Hickman and coworkers [4–7] investigated the partial oxidation of methane using Rh and Pt/alumina monoliths catalysts and proposed that CO and H_2 were the primary products of the methane partial oxidation reaction using these catalysts.

Buyevskaya et al. [19,20] studied the pulse reaction of methane and oxygen over the Rh/Al_2O_3 catalyst using the temporal-analysis-of-product (TAP) reactor. CO_2 was formed as a primary product via a redox mechanism with the surface oxygen of the Rh/Al_2O_3 catalyst. In our apparatus, initially, H_2 formation and carbon deposition probably took place via the decomposition of CH_4 and then deposited carbon or CH_x species generated on the Rh surface were oxidized into CO_x over the Rh and Pd/TiO_2 catalysts. The temperature increase of the rear edge of the catalysts' beds might be caused by the oxidation of CH_x which was formed by an endothermic reaction of methane decomposition. From these results, it seems reasonable even in the presence of O_2, that initially CH_4 decomposed to CH_x and H_2 over the Rh and Pd/TiO_2 catalysts. CH_x on Rh or Pd would be oxidized with gas phase oxygen. Formation of the Rh–CH_x species was confirmed by TPR with H_2 giving CH_4 at above 773 K. H_2 and carbon seemed to be the primary product; however, it cannot accurately be said that CO was the primary product in the partial oxidation of methane in the pulsed reaction over Rh/TiO_2 and Pd/TiO_2 catalysts.

It seems reasonable that measurement of temperature changes of the catalysts' beds reflected only the overall heat change. If the heat loss from the catalyst bed and thermocouples were nil, compared with our present results the estimated temperature decrease in the decomposition of methane would be much larger.

It is possible to induce both exothermic and endothermic reactions anywhere on the catalyst bed. If synthesis gas was formed at the front of the catalyst bed, a slightly exothermic response could be observed. However, endothermic response was detected only at the front edge of the catalyst bed over the Rh and Pd/TiO_2 catalysts. Therefore, as compared to the oxidation of methane, the decomposition of methane when in high concentrations to give carbon or CH_x would proceed easily at the front edge of the catalyst bed over Rh and Pd/TiO_2 catalysts.

Boucouvalas et al. [21,22] reported that synthesis gas produced the over Ru/TiO_2 catalyst was to a large extent formed via the direct partial oxidation scheme. CO and CO_2 were probably formed by parallel routes via two different sites on the catalyst. When the Ru/TiO_2 catalyst was used, a sudden rise in the temperature at the front edge of the catalyst bed was observed upon introduction of the 3 ml pulse of the CH_4 and O_2 mixture (Fig. 9). However, a temperature drop at the front edge of the catalyst bed was observed for a 1 ml pulse of CH_4 and O_2 mixture.

To understand such an unusual behavior, the effect of space velocity was examined in regard to the Ru/TiO_2 catalyst (Fig. 10). When the carrier gas (Ar) flow rate was increased from 10 to 20 and 30 ml/min, a temperature rise at the front edge of the catalyst bed was observed at above 20 ml/min of flow rate, even if 1 ml of pulse was introduced. The temperature rise at the front edge of the catalyst bed increased

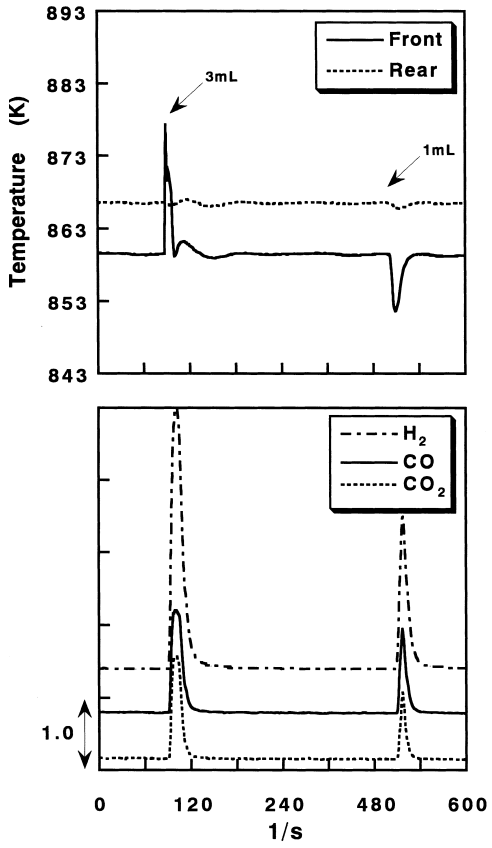

Fig. 9. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Ru(5 wt.%)/TiO_2 catalyst. Reaction conditions — Ar carrier = 10 ml/min, mixed gas: CH_4:O_2 = 2:1, 1 or 3 ml, furnace temperature: 873 K.

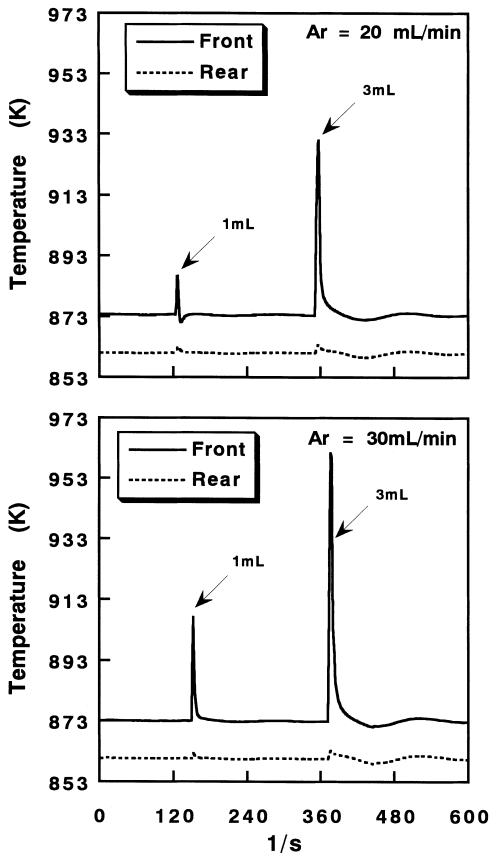

Fig. 10. Temperature profile at front and rear edges of catalyst bed when pulsing CH_4 and O_2 over Ru(5 wt.%)/TiO_2 catalyst. Reaction conditions — Ar carrier = 20 and 30 ml/min, mixed gas: CH_4:O_2 = 2:1, 1 or 3 ml, furnace temperature: 873 K.

with increasing space velocity and amounts of CO and H_2 decreased with increasing space velocity. Probably, complete oxidation of CH_4 would easily occur at high space velocities. In addition, at these space velocities it seemed to be difficult to induce the decomposition of CH_4 and reforming reactions. These results seemed to exhibit two possible synthesis gas formation routes over the Ru/TiO_2 catalyst. The catalytic pathways depended on such reaction conditions as the concentrations of the reactant, space velocity, etc.

The synthesis gas formation route over TiO_2-supported group VIII metal catalysts would basically proceed both by the two-step reactions of the reaction sequence of total oxidation of methane to CO_2 and H_2O (reaction (2)) following the reforming reactions to synthesis gas (reactions (3) and (4)) and by CH_4 decomposition to H_2 and CH_x, following CH_x oxidation to CO_x.

The ratio of combustion reforming to CH_4 decomposition following CH_x oxidation might strongly depend upon the stability of the metal species, the degree of reduction of metal oxides and reaction conditions.

4. Conclusion

A pulsed reaction technique involving measuring of the temperature changes on the catalyst bed afforded useful information regarding the route of synthesis gas formation over the TiO_2-supported group VIII metal catalysts.

The reaction pathway of synthesis gas production over the Ir, Pt and Ni/TiO_2 catalysts seemed to proceed mainly via the two-step reactions that the Ir, Pt and Ni/TiO_2 catalysts might have promoted the reaction sequence of total oxidation of methane to CO_2 and H_2O (reaction (2)), followed by reforming reactions to give synthesis gas (reactions (3) and (4)). In contrast, for the Rh and Pd/TiO_2 catalysts, a different reaction pathway for synthesis gas formation can be proposed. Rh and Pd/TiO_2 catalysts exhibited high catalytic activity in the decomposition of CH_4 to give hydrogen and deposited carbon or CH_x, even in the presence of oxygen. The temperature at the front edge of the catalyst bed decreased upon introduction of a CH_4/O_2 pulse and an increase in the temperature at the rear end was observed, indicating that H_2 formation and carbon deposition probably took place via the decomposition of CH_4, after which deposited carbon or CH_x generated on the Rh surface was oxidized into CO_x.

When the Ru/TiO_2 catalyst was used, a sudden rise in the temperature at the front edge of the catalyst bed was observed upon introduction of the 3 ml pulse of CH_4 and O_2. However, the temperature drop at the front edge of the catalyst bed was observed for a 1 ml pulse of CH_4 and O_2. The catalytic pathways depended upon the stability of metal species, the degree of reduction of metal oxides and the reaction conditions.

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