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Transient Response of Catalyst Bed Temperature in the Pulsed Reaction of Partial Oxidation of Methane to Synthesis Gas over Supported Rhodium and Iridium Catalysts

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Mechanisms of partial oxidation of methane were studied using a pulsed reaction technique and temperature jump measurement. Catalyst bed temperatures were directly measured by introducing a pulse of a mixture of methane and oxygen (2/1). With Ir/TiO_2 catalyst, a sudden temperature increase 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 increased only slightly. The synthesis gas production basically proceeded via a two-step path consisting of highly exothermic methane complete oxidation to give H_2O and CO_2, followed by the endothermic reforming of methane with H_2O and CO_2 over Ir/TiO_2 catalyst. However, with Rh/TiO_2 and Rh/Al_2O_3 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. At first, 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 and then deposited carbon or generated CH_x species would be oxidized into CO_x. However, on Rh/SiO_2, synthesis gas was produced via a two-step path similar to the case of Ir/TiO_2 catalyst. The reaction pathway of partial oxidation of methane with Rh-loaded catalysts depended strongly on the support materials. © 1999 Academic Press

Key Words: **partial oxidation; titania; alumina; pulsed reaction; non-steady-state reaction; support effect.**

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1. INTRODUCTION

Synthesis gas production from methane is indispensable for the chemical utilization of natural gas. Synthesis gas is also important for use in Fischer–Tropsch and methanol syntheses. The following three reactions are of particular industrial interest (1):

Steam reforming:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0_{298} = +206\,\text{kJ/mol} \quad [1]$$

CO_2 reforming:

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

Partial oxidation:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad \Delta H^0_{298} = -36\,\text{kJ/mol} \quad [3]$$

Combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H^0_{298} = -801\,\text{kJ/mol.} \quad [4]$$

Since partial oxidation [3] is a slightly exothermic reaction, it might be operated at a lower temperature to improve thermal efficiency.

Numerous researchers have proposed reaction mechanisms for the partial oxidation of methane (reaction [3]). Two reaction pathways have been proposed to account for the catalytic conversion of methane with oxygen to synthesis gas. The methane combustion [4], followed by steam and CO_2 reformings (reactions [1] and [2]), are commonly accepted mechanisms.

The first report of the partial oxidation of methane to synthesis gas by using supported nickel catalyst was published as early as 1946 by Prettre *et al.* (2). These authors reported that the temperature at the front of the catalyst bed 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 (3, 4). Nakamura *et al.* (5) investigated the same reaction over 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 previously reported that Ir/TiO_2 catalysts has promoted the reaction sequence of total oxidation of methane to CO_2 and H_2O (reaction [4]), as well as the reforming reactions to synthesis gas (reactions [1] and [2]). The CH_4 conversion, and the CO and H_2 selectivities decreased with increasing space velocity, but the CO_2 selectivity increased over Ir/TiO_2 catalyst (6, 7).

The other pathway (reaction [3]) is the direct course. Schmidt *et al.* (8–11) investigated alumina monolith-

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supported rhodium and platinum catalysts for the partial oxidation of methane. The reactions were carried out under adiabatic conditions using 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.* (12, 13) reported that 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.

Buyevskaya *et al.* (14, 15) studied the pulse reaction of methane and oxygen over 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 Rh/Al_2O_3 catalyst. Dehydrogenation of methane yielding carbon deposits on the surface occurred on reduced surface sites.

In this paper, we perform detailed analysis of the reaction pathway of the partial oxidation of methane to synthesis gas using a transient response and pulse reaction technique. Temperature jump measurement was introduced to examine the reaction pathway with supported rhodium and iridium catalysts, and the effects of supports on the methane activation are discussed.

2. EXPERIMENTAL

2.1. Catalysts

The supports used were Al_2O_3, SiO_2 (JRC-ALO-4 surface area, 177 m^2/g; JRC-SIO-4 surface area, 347 m^2/g; reference catalyst provided by the Catalyst Society of Japan), and TiO_2 (Japan Aerosil Co., surface area, 50 m^2/g). The supported rhodium and iridium metal catalysts containing 5 wt% metal were prepared by impregnating aqueous solutions of $RhCl_3 \cdot H_2O$ (Kishida Chemicals) and $IrCl_4 \cdot H_2O$ (Mitsuwa Pure Chemicals) onto a suspended support, followed by evaporation to dryness. Supported catalysts were calcined at 873 K for 5 h in air prior to the reaction.

2.2. Catalytic Activity Measurements

The reaction was carried out with a fixed-bed flow type quartz reactor (i.d. 10 × 350 mm) at atmospheric pressure. Using 60 mg of a catalyst, 25 mL/min CH_4 and 5 mL/min of O_2 were introduced at temperature ranges of 673–873 K.

Prior to the reaction, the catalysts were heated under nitrogen. The reaction temperature was raised in increments of 50 K from 673 to 873 K, and the reaction of CH_4 with O_2 was conducted for 30 min at each temperature. At the end of the reaction period, products (H_2, CO, CH_4, and CO_2) were analyzed using a gas chromatograph directly connected to the outlet of the reaction tube; columns were packed with a Molecular Sieve 5A, 13X and Porapak Q.

2.3. Transient Response of the Pulsed Reactions

Transient response measurement of the catalyst bed temperature in the pulsed reactions were carried out using a fixed bed quartz reactor (i.d. 4 × 200 mm) which was set in a horizontal position in an electric furnace. In the front and the rear end of the catalyst bed, two thin wall sheathed thermocouples (outer diameter 0.6 mm) were set and 100 mg of the catalyst was charged, as shown in Fig. 1. A pulse of CH_4 and O_2 (2/1) or CO_2 (1/1) mixed gas was introduced with a six-port gas sampling valve equipped with measuring tubes, under a stream of Ar carrier gas. Before the reaction, the catalysts were reduced with H_2 flow for 60 min at 873 K. The reaction temperature was controlled by monitoring the outside temperature of the reactor wall by using a programmable controller.

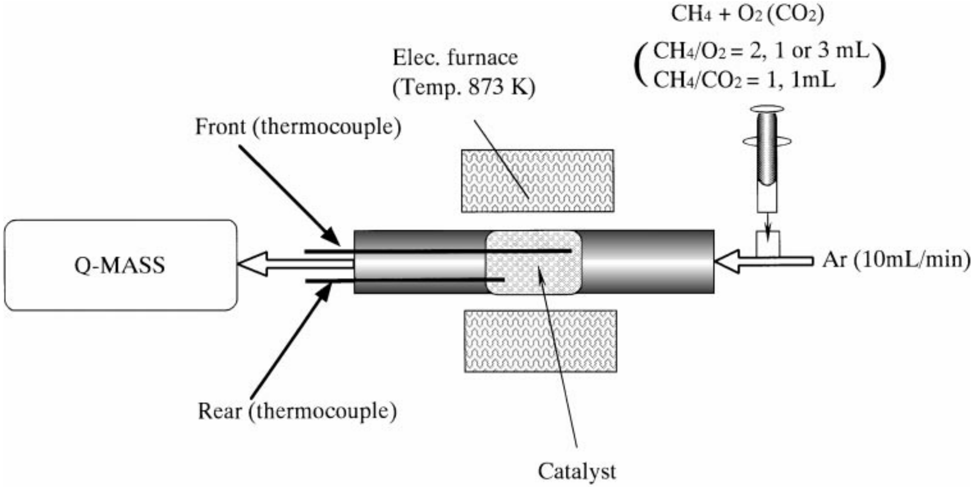


FIG. 1. Schematic representation of the flow reactor measuring temperature jump.

Analyses of the gases during the pulsed reactions were made using an on-line quadruple mass spectrometer (HAL201, Hiden Analytical Ltd.). 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.

Transmission electron microscope (TEM) was performed using a Hitachi H-9000 instrument on fresh and used catalyst samples so that the morphology of the deposited carbon could be determined.

3. RESULTS

3.1. *Effect of TiO_2-Supported Rhodium and Iridium Metals on the Performance of Partial Oxidation of Methane*

The effect of reaction temperature on the product concentrations during partial oxidation of methane with Rh (5 wt%)/TiO_2 and Ir(5 wt%)/TiO_2 catalysts are shown in Figs. 2a and 2b. TiO_2 was used as a support of Rh and Ir loaded catalysts, since Ir/TiO_2 catalyst afforded a high CH_4 conversion to synthesis gas and the initial activity of this catalyst was maintained for a long period. Both Ir and Rh catalysts showed a high catalytic activity at 873 K for the formation of synthesis gas and afforded almost the same product concentrations at above 823 K. Below 773 K, however, Rh/TiO_2 catalyst produced a higher concentration of H_2 than Ir/TiO_2 catalyst.

According to the thermodynamics reported for the methane and oxygen system ($CH_4 : O_2 = 2:1$) (1), the formations of CO_2 and H_2O are dominant at temperatures lower than about 823 K and the synthesis gas formation becomes favorable at higher temperatures. Temperatures higher than 923 K are thermodynamically required for a high methane conversion (>90%) and a high synthesis gas selectivity (>90%). Such an equilibrium limitation might be the reason for the observed lower methane conversion of 25% at 873 K (Fig. 2). At 873 K, reactions [3] and [4] seem to occur. If one assumes that the equilibrium concentration ratio of CO/CO_2 is about 4, methane conversion can be calculated as about 25%. This value agreed with experimental results.

TABLE 1

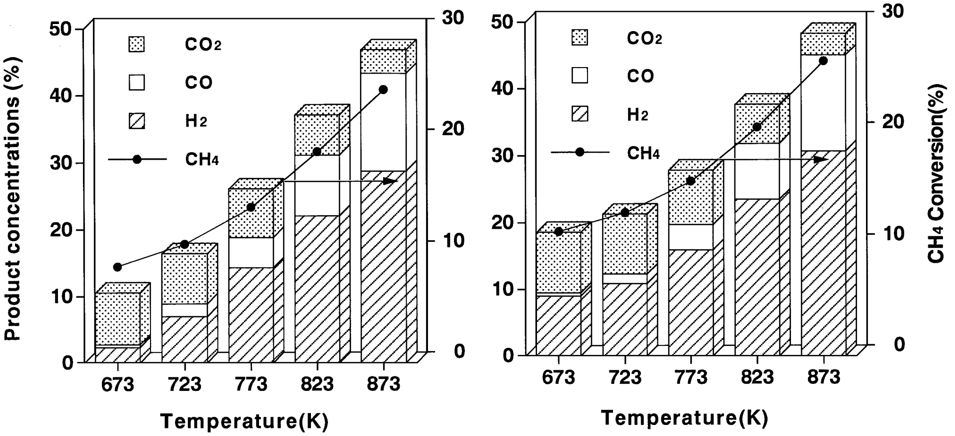
Effect of Space Velocity on the CH_4 Conversion and Product Selectivities

Catalyst	SV (h^{-1} mL/g-cat)	Conversion CH_4 (%)	Selectivity CO (%)	Selectivity CO_2 (%)	Selectivity H_2 (%)	H_2/CO ratio
Ir/TiO_2	30,000[a]	25.7	81.8	18.2	83.1	2.0
	60,000	21.6	69.2	30.8	73.6	2.1
	90,000	20.5	65.5	34.5	69.4	2.1
Rh/TiO_2	30,000[a]	26.5	81.6	18.4	87.3	2.1
	60,000	22.3	64.8	35.2	78.7	2.4
	90,000	23.0	65.5	34.5	77.1	2.4

Note. Catalyst: 60 mg; metal loading level = 5 wt%; $CH_4/O_2 = 5.0$; reaction temperature, 873 K.

[a] Reference (6).

Table 1 shows the effect of space velocity on the CH_4 conversion and product selectivities at 873 K. When Ir/TiO_2 catalyst was used, the CH_4 conversion and the CO and H_2 selectivities decreased with increasing space velocity, but CO_2 selectivity increased. Although the differences in the CH_4 conversion was not large, change in the CO_2 selectivity was significant, and such differences are much larger than experimental errors. On the other hand, Rh/TiO_2 catalyst maintained constant CH_4 conversions and high H_2 selectivities over the range of space velocities examined. Rh/TiO_2



Ir(5wt%)/TiO2

Rh(5wt%)/TiO2

FIG. 2. Effect of temperature on the product concentrations over TiO_2-supported Ir(5 wt%) and Rh(5 wt%) catalysts: (▩) CO_2, (□) CO, (▨) H_2, (●) CH_4. Reaction conditions: $CH_4 : O_2 = 5:1$, flow rate = 30 mL/min; catalyst: 60 mg, SV = 30,000 h^{-1} mL/g-catalyst.

catalyst also showed higher H_2 selectivity and H_2/CO ratio than Ir/TiO_2 catalyst.

3.2. *Decomposition of Methane over Rhodium and Iridium-Loaded Catalyst*

Figure 3 shows the transient response of H_2 production when the flowing gas was switched from Ar to CH_4 at 873 K (reaction [5]) over Rh(5.0 wt%)/TiO_2 and Ir(5 wt%)/TiO_2 catalysts. H_2 was the only gaseous species observed (no higher hydrocarbons):

$$CH_4 \rightleftarrows C + 2H_2 \qquad \Delta H^0_{298} = +75\ \text{kJ/mol.} \qquad [5]$$

When CH_4 was supplied to Ir/TiO_2 catalyst, a slight H_2 response appeared instantaneously and then decreased to a low level. On the other hand, methane decomposition continued to give H_2 over Rh/TiO_2 catalyst for 2400 s. These results show that Rh/TiO_2 exhibited a much higher activity toward the decomposition of CH_4 than did Ir/TiO_2.

In order to investigate the effect of support of Rh loaded catalysts on the decomposition of CH_4, Rh(5.0 wt%)/Al_2O_3 and Rh(5.0 wt%)/SiO_2 catalysts were tested. As shown in Fig. 4, Rh(5.0 wt%)/Al_2O_3 catalyst initially showed a high activity toward decomposition of CH_4. However, the concentration of H_2 gradually decreased with increasing time on stream and H_2 production was not detected after 4800 s. Verykios *et al.* (16) reported similar results 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 the initial rate. Rh(5.0 wt%)/SiO_2 catalyst exhibited behavior similar to that of Ir/TiO_2 catalyst.

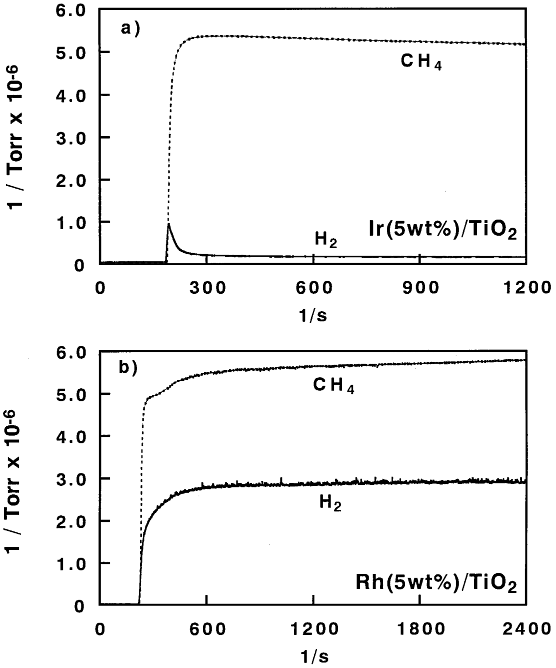


FIG. 3. Decomposition of CH_4 over TiO_2-supported Ir(5 wt%) and Rh(5 wt%) catalysts. Reaction conditions: reaction temperature, 873 K; catalyst, 100 mg; CH_4 flow rate, 10 mL/min; 1 Torr = 133.3 N m^{-2}.

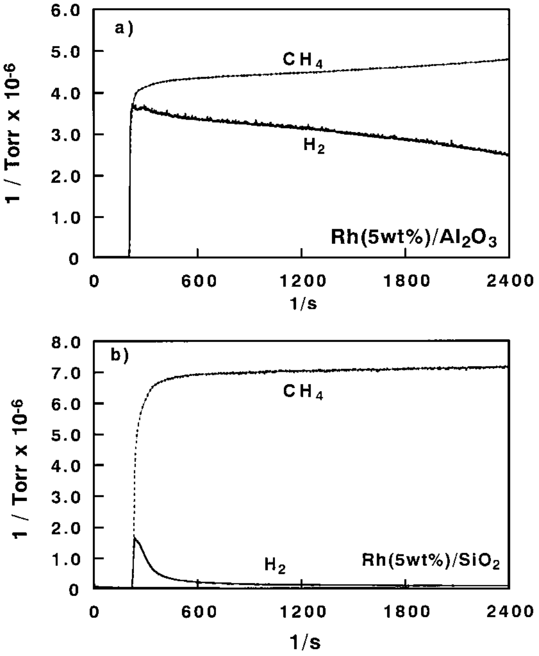


FIG. 4. Decomposition of CH_4 over supported Rh(5 wt%) catalysts. Reaction conditions: reaction temperature 873 K; catalyst, 100 mg; CH_4 flow rate, 10 mL/min; 1 Torr = 133.3 N m^{-2}.

Figures 5, 6, and 7 show transmission electron microscope (TEM) images of Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2 catalysts fresh and after the reaction for 2400 s. No specific carbon formation was observed on Ir/TiO_2 catalyst. On the other hand, Rh/TiO_2 catalyst clearly showed formation of a "whisker" type carbon (Fig. 5b). This type of carbon has also been observed on the steam and carbon dioxide reforming catalysts, and particularly on nickel catalyst (1, 17, 18). Whisker carbon formation did not alter the rate of H_2 production. In our case, no deactivation of the Rh/TiO_2 catalyst for methane decomposition was observed with carbon deposition during the reaction for 2400 s. Whisker type carbon was not formed on Rh/Al_2O_3 catalyst (Fig. 6b), but probably "encapsulate" type carbon would be formed (19), since formation of H_2 gradually decreased with increasing time on stream and H_2 production ceased after 4800 s. The encapsulate form of carbon has been reported to build up with time and to deactivate the catalyst by covering the nickel surface for partial oxidation of CH_4 (19). On Rh/SiO_2 catalyst, no type of carbon species was observed, due to the small activity for CH_4 decomposition (Fig. 7b). These results indicate that the catalytic activities of CH_4 decomposition and deposited carbon species over the Rh loaded catalysts depended strongly on support materials.

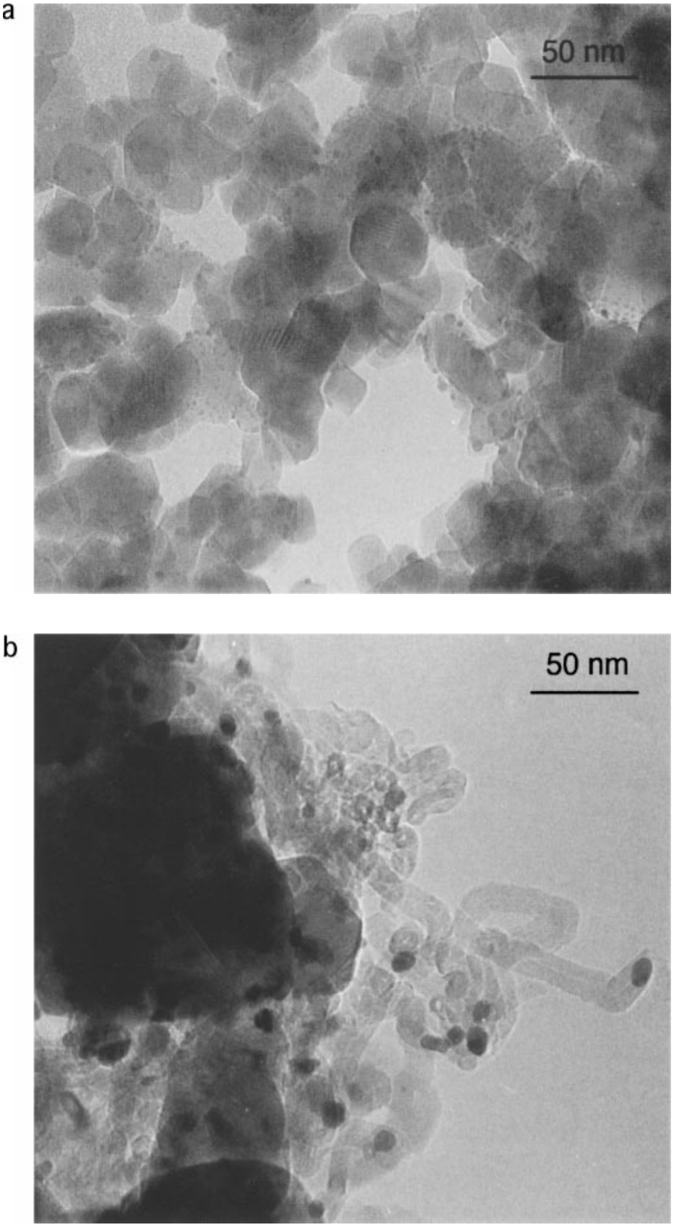


FIG. 5. Transmission electron microscope (TEM) showing the deposited carbon on the surface of the Rh(5 wt%)/TiO_2 catalyst: (a) fresh, (b) after reaction.

3.3. *Transient Response of Catalyst Bed Temperature in the Pulsed Reaction of Partial Oxidation of Methane*

To investigate the mechanisms of partial oxidation of methane over supported rhodium and iridium catalysts, a pulsed reaction technique was employed to measure transient temperature changes in the catalysts beds.

First, in order to prove the validity of this method, a simple endothermic reaction for CO_2 reforming was examined. Fig. 8 shows the transient temperature responses of Ir/TiO_2 catalyst against a pulsed injection of CH_4/CO_2. The temperature at the front edge decreased with the introduction of CH_4/CO_2 pulse, and a slight decrease in the temperature of the rear end of the catalyst bed was observed. The decrease in the catalyst bed temperature increased with increasing amounts of reactant introduced. Since the total flow rate was kept constant during the introduction of mixed gas, this temperature decrease could not be ascribed to the increase in the cold gas flow rate, but could safely be ascribed to endothermic reaction. Thus, the validity of this measurement for the test of endo- or exothermic reactions was confirmed.

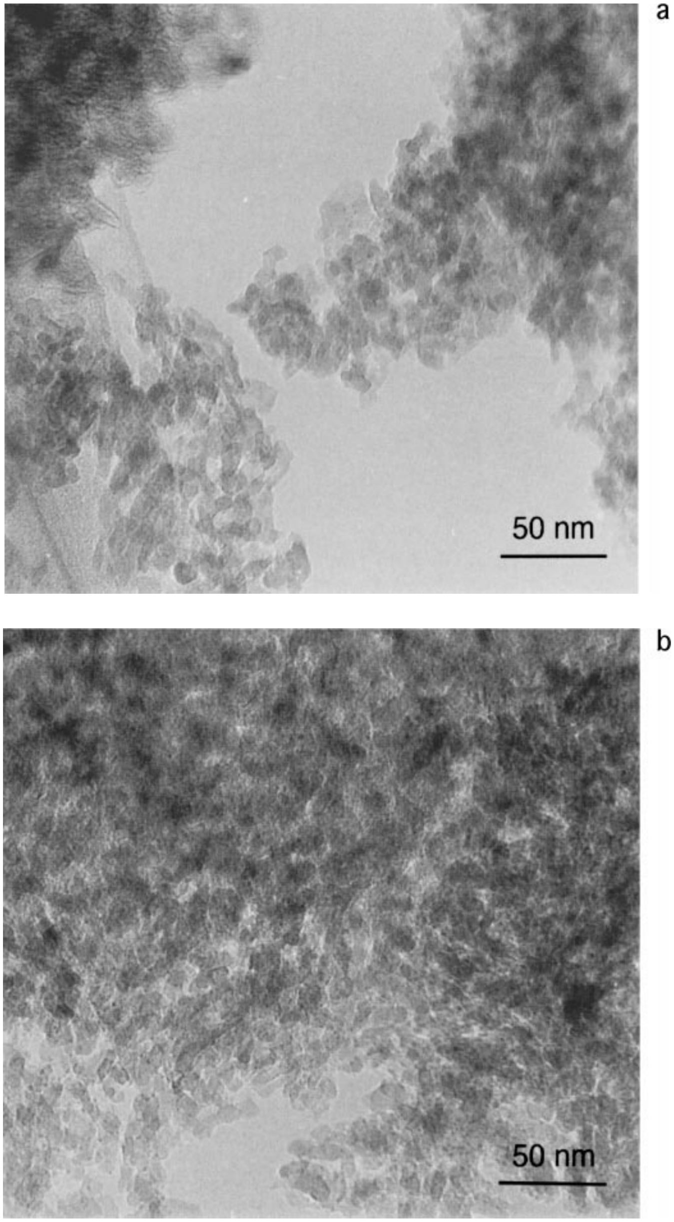


FIG. 6. Transmission electron microscope (TEM) showing the deposited carbon on the surface of the Rh(5 wt%)/Al_2O_3 catalyst: (a) fresh, (b) after reaction.

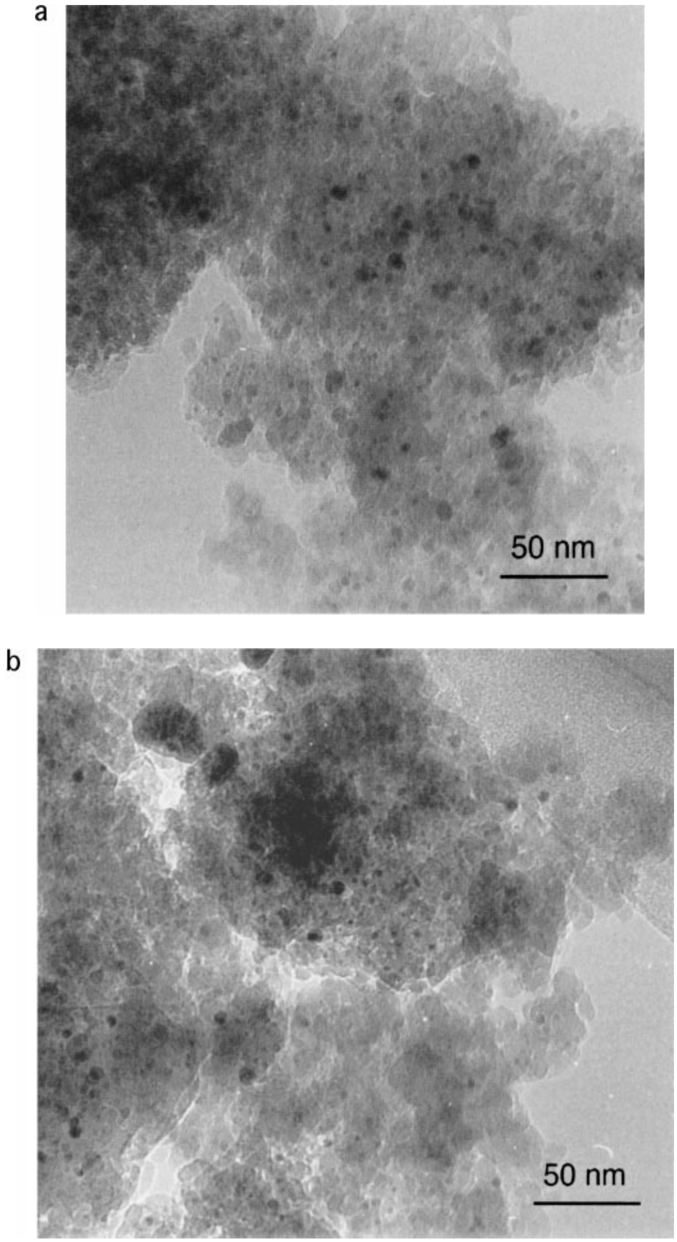


FIG. 7. Transmission electron microscope (TEM) showing the deposited carbon on the surface of the Rh(5 wt%)/SiO_2 catalyst: (a) fresh, (b) after reaction.

Among the four reactions, [1] and [2] are highly endothermic, [3] is moderately exothermic, and [4] is highly exothermic. Observation of the catalyst bed temperature by means of injecting a pulse of reactants may provide information about the reaction taking place at the catalyst bed.

Catalyst bed temperature was directly measured by introducing a pulse of a mixture of methane and oxygen. Figures 9, 10, 11, and 12 show the transient temperature responses of Ir/TiO_2, Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2 catalysts against a pulsed injection of CH_4/O_2, together with the effluent composition. Difference in the product intensities varying with pulse size or catalysts (Figs. 8–12) might be caused by differences in activities of each catalyst. Product peak area and temperature response were changed by varying with pulse size.

When Ir/TiO_2 catalyst was used, a sudden rise in temperature 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. Similar phenomena have also been observed in a conventional fixed-bed continuous flow system by other researchers (3, 4).

However, when Rh/TiO_2 and Rh/Al_2O_3 catalysts were used, the temperature at the front edge decreased upon introduction of the CH_4/O_2 pulse, and an increase in the temperature at the rear end was observed. Reproducibility of temperature changes of the catalyst bed was confirmed by changing carrier gas, Ar, flow rate from 10 to 40 mL/min. At each Ar flow rate, similar temperature drops at the front edge were observed over Rh/TiO_2 catalyst. Since exothermic peaks were observed at the rear edge of the catalyst beds in the cases of Rh/TiO_2 and Rh/Al_2O_3

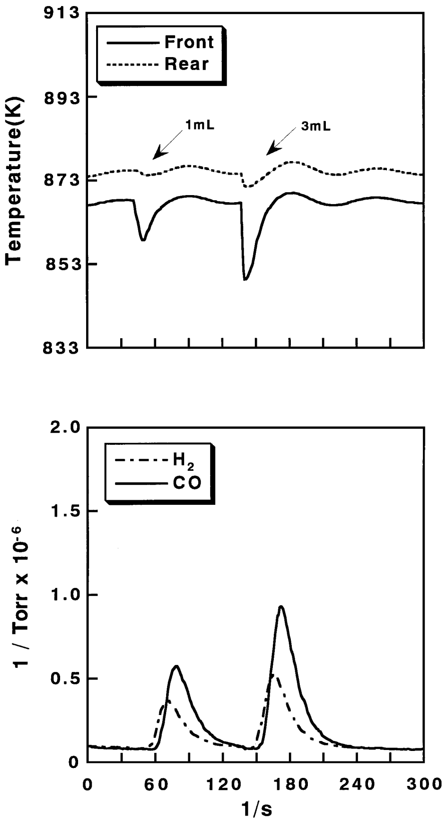


FIG. 8. Temperature profile at front and rear edges of the catalyst bed and the responses of products when pulsing CH_4 and CO_2 over Ir(5 wt%)/TiO_2 catalyst. Reaction conditions: Ar carrier, 10 mL/min; mixed gas, $CH_4 : CO_2 = 1 : 1$, 1 or 3 mL; furnace temperature, 873 K; 1 Torr = 133.3 N m^{-2}.

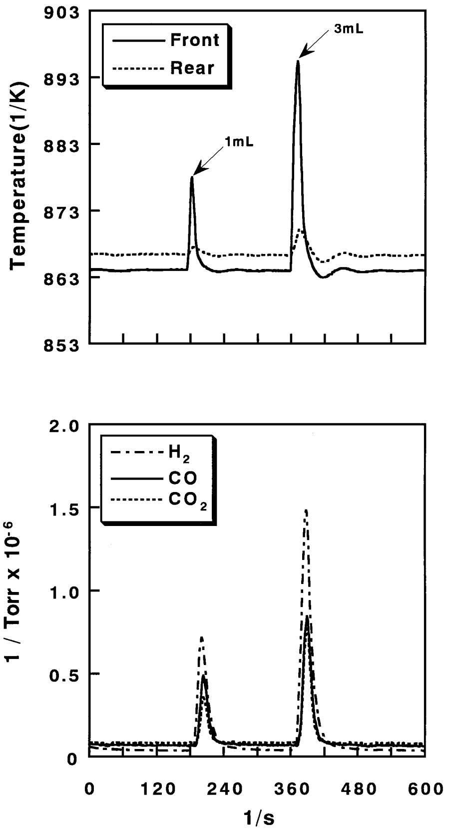


FIG. 9. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Ir(5 wt%)/TiO_2 catalyst. Reaction conditions: Ar carrier, 10 mL/min; mixed gas, $CH_4 : O_2 = 2 : 1$, 1 or 3 mL; furnace temperature, 873 K; 1 Torr = 133.3 N m^{-2}.

catalysts, it seemed unlikely that exothermic reaction would occur before the thermocouple at the front edge of the catalyst bed in the cases of Rh/TiO_2 and Rh/Al_2O_3 catalysts. On the other hand, Rh/SiO_2 showed a rise in temperature at the front edge of the catalyst bed upon introduction of the pulse.

In each of the catalysts used, H_2, CO, and CO_2 were obtained. In all cases, temperature changes increased with increasing amount of pulsed reactant gas. During the measurement of temperature changes, an effluent was analyzed by a Q-mass spectrometer. In all cases, unreacted CH_4, CO, H_2, and CO_2 were detected. The amount of CO_2 was higher than that in the steady reaction.

4. DISCUSSION

The reaction pathway of synthesis gas production over the Ir(5 wt%)/TiO_2 catalyst seemed to proceed via the two-step reactions that Ir/TiO_2 catalyst might have promoted the reaction sequence of total oxidation of methane to CO_2 and H_2O (reaction [4]) and reforming reactions to synthesis gas (reactions [1], [2]). This was previously supported by the dependence of catalytic activity on the support materials, in relation with the partial oxidation of methane and the CO_2 reforming. Furthermore, when Ir/TiO_2 catalyst was used, the CH_4 conversion and the CO and H_2 selectivities decreased with increasing space velocity, but CO_2 selectivity increased (Table 1). These results again indicate that the slower CO_2 reforming reaction was suppressed to give a large amount of unreacted CO_2.

When Ir/TiO_2 and Rh/SiO_2 catalysts were used, a sudden rise in temperature at the front edge of the catalyst bed was observed upon introduction of the pulse of CH_4 and O_2, but the temperature of the rear end of the catalyst bed was only slightly increased (Figs. 9 and 12). If the heat loss from the catalyst bed and thermocouples were nil, the estimated temperature increase in the complete oxidation would be ca. 200 K for the 3-mL pulse. In our apparatus, heat loss could not be eliminated. The observed temperature rise was about 30 K. As seen in Fig. 8, the temperature decrease in the CO_2 reforming was ca. 20 K. The difference in the heat of reaction between exothermic combustion and endothermic CO_2 reforming was significantly large, as compared to the observed temperature differences. Endothermic CO_2

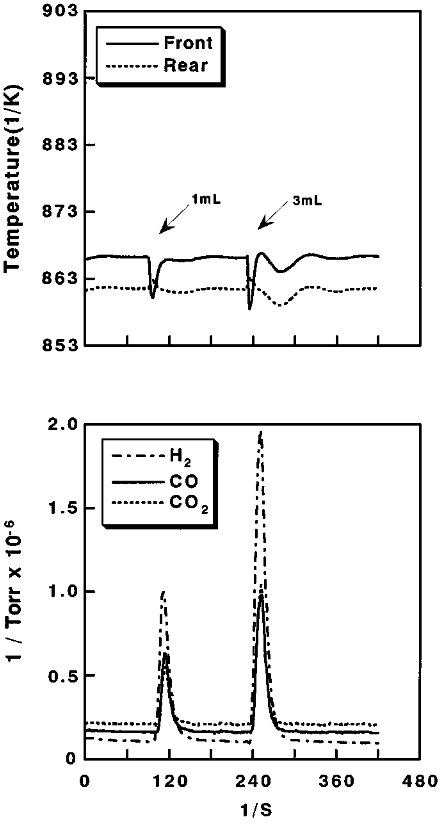


FIG. 10. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Rh (5 wt%)/TiO_2 catalyst. Reaction conditions: Ar carrier, 10 mL/min; mixed gas, $CH_4 : O_2 = 2 : 1$, 1 or 3 mL; furnace temperature, 873 K; 1 Torr = 133.3 N m^{-2}.

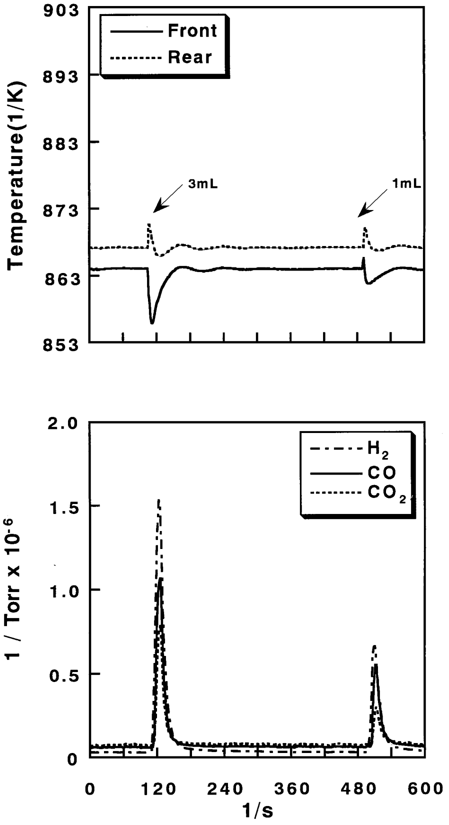


FIG. 11. Temperature profile at front and rear edges of catalyst bed and the responses of products when pulsing CH_4 and O_2 over Rh (5 wt%)/Al_2O_3 catalyst. Reaction conditions: Ar carrier, 10 mL/min; mixed gas, $CH_4:O_2 = 2:1$, 1 or 3 mL; furnace temperature, 873 K; 1 Torr = 133.3 N m^{-2}.

and H_2O reforming reactions proceeded to induce not only heat loss from the reactor wall, but also a decrease in the rise in temperature of the catalyst bed. If a direct partial oxidation reaction [3] proceeded, due to the small degree of heat generation such a large rise in temperature could not be observed. Thus, when Ir/TiO_2 and Rh/SiO_2 were used, the temperature increase in the front edge of the catalyst bed could safely be ascribed to the complete oxidation of methane. The results for the Rh/SiO_2 catalyst are consistent with the proposed mechanism by Nakamura *et al.* (5), although these authors did not provide evidence for this mechanism.

It is surprising that the temperature drop at the front edge of the catalyst bed was observed for both Rh/TiO_2 and Rh/Al_2O_3, even when methane and oxygen were introduced in a ratio of 2 to 1. In the steady flow, Rh/TiO_2 catalyst maintained high H_2 selectivities at the high space velocity (Table 1). Rh/TiO_2 and Rh/Al_2O_3 catalysts had a high activity for decomposition of CH_4 (Figs. 3 and 4). Under the high space velocity, Hickman *et al.* (8–11) investigated the partial oxidation of methane using Rh and Pt/alumina monolith catalysts. They proposed that CO and H_2 were the primary products of the methane partial oxidation reaction with these catalysts. Buyevskaya *et al.* (14, 15) studied the pulse reaction of methane and oxygen over Rh/Al_2O_3 catalyst using the TAP reactor. CO_2 was formed as a primary product via a redox mechanism with the surface oxygen of Rh/Al_2O_3 catalyst. In our apparatus, at first, 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 Rh/TiO_2 and Rh/Al_2O_3. H_2 and carbon seemed to be the primary product; however, it was difficult to say that CO was the primary product in the partial oxidation of methane in the pulse reaction over Rh/TiO_2 and Rh/Al_2O_3. It seems to be reasonable that measurement of temperature changes of catalysts bed reflected only the overall heat change. If the heat loss from the catalyst bed and thermocouples were nil, compared with the our present results, the estimated temperature decrease in the decomposition of methane would be much larger. It is possible that both exothermic and endothermic reactions could occur anywhere in the catalyst bed. If synthesis gas was formed at the front of the catalyst bed, a slightly exothermic response could be

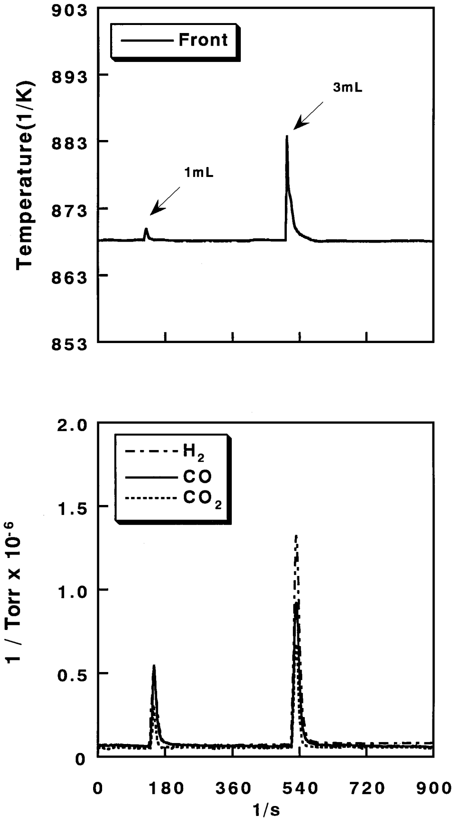


FIG. 12. Temperature profile at front edge of catalyst bed and the responses of products when pulsing CH_4 and O_2 and Rh(5 wt%)/SiO_2 catalyst. Reaction conditions: Ar carrier, 10 mL/min; mixed gas, $CH_4:O_2 = 2:1$, 1 or 3 mL; furnace temperature, 873 K; 1 Torr = 133.3 N m^{-2}.

observed. However, an endothermic response was detected only at the front edge of the catalyst bed over Rh/TiO_2 and Rh/Al_2O_3 catalysts. Therefore, in the high methane concentration, compared to the oxidation of methane, decomposition of methane to give carbon or CH_x would easily proceed at the front edge of the catalyst bed over Rh/TiO_2 and Rh/Al_2O_3 catalyst.

Boucouvalas *et al.* (12, 13) reported that synthesis gas 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 of the catalyst.

When 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 1-mL pulses of CH_4 and O_2. These results seemed to exhibit two possibilities of synthesis gas formation routes over Ru/TiO_2 catalyst. Catalytic pathways depended on the reaction conditions such as concentrations of the reactant and flow rates.

The slight temperature increase of the rear edge of the catalyst bed on Ir/TiO_2 catalyst might be ascribed to the heat conduction from the front and middle part of the catalyst bed. Synthesis gas formation over Ir/TiO_2 catalyst would proceed basically via the two-step path. Methane combustion would occur in the front edge of the catalyst bed. Since a large amount of unreacted CO_2 was observed, the total heat of the reaction would be exothermic.

On the other hand, when Rh/TiO_2 and Rh/Al_2O_3 catalysts were used, the temperature increase of the rear edge of the catalyst bed might be caused by oxidation of unreacted methane, CH_x, H_2 which were made from the decomposition of methane or oxidation of reduced Rh metal could be possible due to a high concentration of oxygen. Probably, hydrogen was produced mainly by decomposition of CH_4 on the front edge of the catalyst bed, and then generated H_2 and CH_x species were oxidized into H_2O and CO_x in the Rh/TiO_2 and Al_2O_3 catalysts.

5. CONCLUSION

A pulsed reaction technique of measuring the temperature jump of the catalyst bed afforded strong support that synthesis gas was formed via a two-step reaction pathway, which consisted of methane complete oxidation to give H_2O and CO_2, followed by the reforming of methane with steam and CO_2 for Ir/TiO_2 and Rh/SiO_2 catalysts.

On the other hand, when Rh/TiO_2 and Rh/Al_2O_3 catalysts were used, a different reaction pathway for synthesis gas formation can be proposed. Rh/TiO_2 and Rh/Al_2O_3 catalysts exhibited a 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 deposition of carbon probably took place via decomposition of CH_4, and then deposited carbon or CH_x generated on the Rh surface was oxidized into CO_x. In the case of Rh-loaded catalysts, the reaction pathway depended strongly on the support materials.

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