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Reactivity of Carbon Species Formed on Supported Noble Metal Catalysts in Methane Conversion Reactions

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The reactivity of carbon species formed from methane decomposition over supported noble metal catalysts was examined. In the Ru-loaded case, the rate of formation of CH_x species in the decomposition of CH_4 and the amount of CH_x species over Ru are independent of the type of support. However, the carbon species on Ru/La_2O_3 seems to be more uniform and reactive than that on Ru/Al_2O_3. After the decomposition of CH_4 over Ru-loaded catalysts was carried out at 700°C, a temperature-programmed reaction with D_2 was carried out. CD_4 was the major product on all the supports, and only slight amounts of CH_3D, CH_2D_2, and CHD_3 were detected over La_2O_3, ZrO_2, and Y_2O_3 supports. The reactivity of CH_x species on Ru strongly depends on the supports. The reactivity of CH_x species on Ru and Rh loaded on La_2O_3 can be divided into two categories. These categories are not based on the differences in the number of x in CH_x species. On Ru, x in the CH_x species is equal to nearly 0, with a very small portion having $x = 2$. On the other hand, x is almost exclusively 0 on Rh. It seems that Rh leads to a higher rate of decomposition for methane than does Ru.

Key Words: **temperature-programmed reaction; temperature-programmed oxidation; ruthenium; rhodium; iridium; lanthanum oxide.**

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1. INTRODUCTION

Recently, increasing attention has been paid to the conversion of methane to synthesis gas. The partial oxidation and CO_2 reforming of methane have attracted much attention (1–5):

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

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

It is of interest to shed light on the mechanistic aspects of the partial oxidation and CO_2 reforming of CH_4 on the supported transition-metal catalyst. Methane is believed to be adsorbed and dissociated on transition metal surfaces such as Ni (6), Ru (7), Rh (7–9), Pd (7, 10), Pt (7), and Ir (7), as shown by

$$CH_4\ \text{ad.} \rightarrow CH_x\ \text{ad.} + (4 - x)/2H_2. \qquad [3]$$

Osaki *et al.* have confirmed through a pulse reaction-rate analysis the dissociative adsorption of CH_4, which results in the release of H_2 on supported Ni or Co catalysts (11, 12).

Solymosi and co-workers have reported that a supported Rh catalyst is active in the decomposition of CH_4 to give H_2, together with a small amount of C_2H_6 and carbonaceous residues. Three different types of carbon having different reactivities on Rh have been distinguished, following CH_4 decomposition, by means of the H_2 temperature-programmed reaction technique (8). Adsorbed CH_3 reacted with CO_2 over Rh/SiO_2 at and above 100°C to give CO. The authors concluded that CH_4 fragments formed in the decomposition of CH_4 afforded CH_x species, and it reacted with CO_2 during CO_2 reforming of CH_4 over supported Rh catalysts (9).

Mark *et al.* have reported that the activity of Ru, Rh, and Ir catalysts in the CO_2 reforming of CH_4 could be correlated with the accessible metal surface area and that there is no detectable effect of the pore structure or nature of the support on the reaction rate (13).

Methane can be activated thermally over supported Group VIII metals to produce carbonaceous species that react with hydrogen to produce C_2 (14, 15). Similar studies have been reported by Amariglio and co-workers (16, 17) and Solymosi *et al.* (18, 19). The dissociative adsorption of methane occurs at temperatures above 100°C and produces three forms of carbon with different reactivities.

Carstens and Bell have reported that three types of carbon are formed similarly over a Ru/SiO_2 catalyst and that the proportion among these species depends on the total carbon coverage and the length of time that the carbon has been aged at a given temperature after deposition (20).

CH_x species formed on the metal surface vary with the support used even if the same metal is employed (4, 9).

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We have reported in previous papers that the performance of supported iridium catalysts depends strongly upon the support materials in the partial oxidation of methane to synthesis gas (21) and that the interaction between CO_2 and the support strongly affects the reactivity of ruthenium catalysts in the CO_2 reforming of methane (22). In the pulsed reaction of partial oxidation and CO_2 reforming of methane to synthesis gas, the mechanism of synthesis gas formation over group VIII transition metal loaded catalysts was strongly affected by loaded metal species and support materials (23–25).

This paper deals with temperature-programmed reactions with H_2 and O_2 as well as the transient response reactions of CH_4, in order to examine the activation of the C–H bond and the reactivity of CH_x species on noble metals loaded on various supports.

2. EXPERIMENTAL

2.1. *Materials*

As a support for γ-Al_2O_3, ALO-4 (supplied from the Catalyst Society of Japan), ZrO_2 (Japan Aerosil Co.), Y_2O_3 (Nacalai Tesque, Inc.), and La_2O_3 (Wako Pure Chemical Industries Ltd.) were used. All chemicals were used without further purification.

Noble-metal-loaded catalysts were prepared by impregnating an acetone solution of $RuCl_3 \cdot nH_2O$, $RhCl_3 \cdot nH_2O$, $IrCl_4 \cdot nH_2O$ (Mitsuwa Kagaku Co.) to yield 0.5 or 5.0 wt% on various supports. All the catalysts were dried under reduced pressure, calcined in air at 550°C for 5 h, and pelletized and sieved to a size between 60 and 100 mesh.

2.2. *Apparatus and Procedure for the Pulse–Response Reaction*

All reactions were performed using a fixed-bed quartz reactor having an internal diameter of 4 mm and a length of 200 mm, and the reactor was set in a horizontal position in an electric furnace. Quartz wool plugs were packed in the center part of the reactor and 50 mg of the catalyst was charged. Before the reaction, the catalysts were reduced under H_2 flow for 60 min at 600°C. CH_4, H_2, D_2, and O_2 were used without purification. The reaction temperature was controlled by monitoring the outside temperature of the reactor with chromel alumel thermocouples using a programmable controller.

The transient response reaction, temperature-programmed reduction (TPR), and oxidation (TPO) were performed with an on-line quadrupole mass spectrometer (HAL201, Hiden Analytical Ltd.). The mass spectrometer scanned corresponding parent peaks of 11 components, H_2, D_2, HD, CH_4, CH_3D, CH_2D_2, CHD_3, CD_4, H_2O, CO, and CO_2, within 1 s, and repeated scans were collected with a personal computer.

3. RESULTS AND DISCUSSION

In the CO_2 reforming of methane, the interaction between CO_2 and the support, as well as the activation of methane on the Ru surface, has been discussed in a previous paper (23). The results are summarized as follows: La_2O_3, Y_2O_3, and ZrO_2, which showed a high level of activity, and Al_2O_3, commonly used in the reforming reaction, were compared when they were loaded with Ru. After CO_2 was fed at 600°C, a pulse of CH_4 under a steady Ar flow was introduced over a Ru/La_2O_3 catalyst. We observed the response of CO that was generated from the reaction with CH_x on the ruthenium and the Ru-Ox formed during CO_2 treatment or during the reaction of Ru-CH_x with adsorbed CO_2 onto the La_2O_3. Over Ru/Al_2O_3 catalyst, however, a very small response of CO was observed. A pulse of $^{13}CO_2$ was introduced under steady CH_4 flow over Ru/La_2O_3, Ru/Y_2O_3, and Ru/ZrO_2 catalysts. Symmetrical ^{13}CO responses were observed, but a small response of ^{12}CO from $^{12}CH_x$ continued to evolve after generation of ^{13}CO from $^{13}CO_2$ ceased. The following reaction cycle is believed to occur in the CO_2 reforming of methane on active supports: A part of metallic ruthenium reacted with CH_4 to give Ru-CH_x; simultaneously ruthenium metal could be oxidized with CO_2 to give Ru–O_x and CO, and then, oxygen transfer from Ru–O to Ru–CH_x took place to give CO and metallic ruthenium.

The effect of the support on the reactivities of CH_x species formed on noble-metal-loaded catalysts is another important factor controlling the catalytic activity. This factor was examined by temperature-programmed reactions.

3.1. *Responses of H_2 Production to the Decomposition of CH_4*

Figure 1 shows the transient response reaction after switching from Ar to CH_4 for 5 min at temperatures of 600, 700, and 800°C on Ru (5.0 wt%)/La_2O_3 and Ru (5.0 wt%)/Al_2O_3 catalysts. When CH_4 was supplied, the response of H_2 formation to the decomposition of methane was immediately observed, indicating that the dissociation to hydrogen and carbonaceous species (CH_x) is rapid. However, the concentration of H_2 decreased gradually within 5 min. A similar result has been reported by Verykios and co-workers (26) over Rh/Al_2O_3 catalyst at 650°C. They concluded that after 10 min of a stream of CH_4, the rate of H_2 production decreased to one-seventh of the initial rate (26).

The amount of H_2 produced at 600°C in 5 min is almost the same as the amount of loaded ruthenium species (Table 1), indicating that x in the CH_x species formed over the ruthenium active site is probably large. The surface area of Ru/La_2O_3 ($SA = 3.6\ m^2/g$) is smaller than that of Al_2O_3 ($SA = 174\ m^2/g$), and dispersion of ruthenium on La_2O_3 would probably be poor compared to that on Ru/Al_2O_3

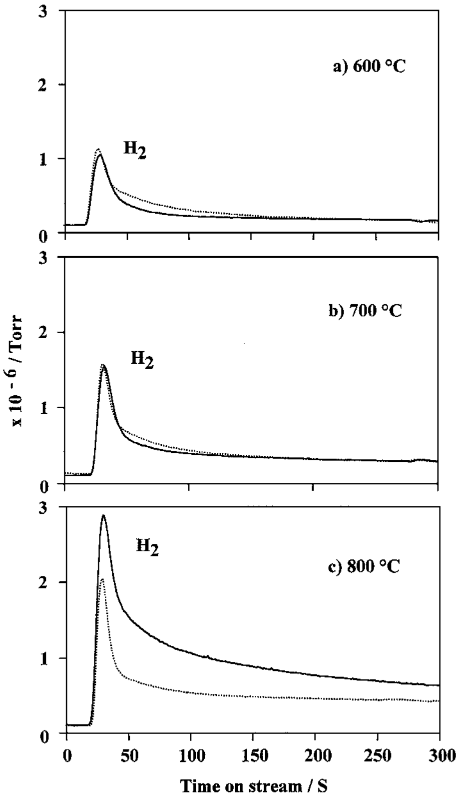

FIG. 1. Response of H_2 production. (—) Ru/La_2O_3: (···) Ru/Al_2O_3. Reaction conditions: catalyst 50 mg, flow rate of CH_4, 10 mL/min, 1 Torr = 133.3 Nm^{-2}.

catalyst. However, a large amount of H_2 was generated at 800°C over the Ru/La_2O_3 catalyst, and the amount of H_2 was more than four times that of the Ru species. Although the dispersion of Ru was not determined, the formation of such a large amount of hydrogen seems to indicate that carbon growth does occur on the Ru center.

3.2. Transient Response Reactions and Temperature-Programmed Reactions with O_2

To evaluate the amounts of carbon species formed on Ru during the treatment of CH_4 from 600 to 800°C; at each temperature, a transient response reaction was carried out with oxygen at the same temperature as CH_4.

TABLE 1

Amount of H_2 Production in CH_x Formation

Run	Catalyst	Reaction temperature (°C)	Amount of H_2 (×10^{-2} mmol)
1	Ru/La_2O_3	600	2.94
2		700	6.33
3		800	19.41
4	Ru/Al_2O_3	600	3.75
5		700	6.08
6		800	9.62

Note. Catalyst, 50 mg; loading level of Ru = 5.0 wt% (2.47 × 10^{-2} mmol); flow rate of CH_4 = 10 ml/min for 5 min.

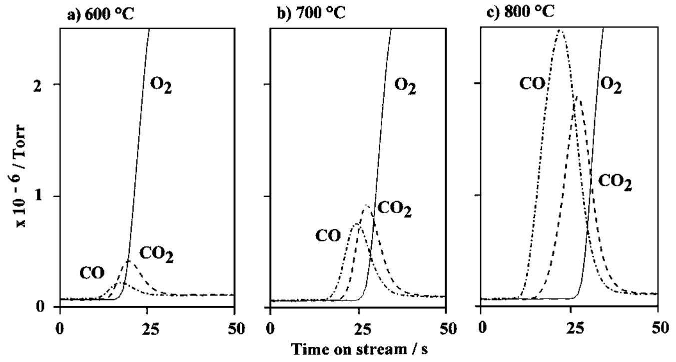

FIG. 2. Transient response of O_2 flow after CH_4 decomposition on Ru/La_2O_3 at three different temperatures. Reaction conditions: catalyst, Ru (5 wt%)/La_2O_3 (50 mg), flow rate of CH_4, 10 mL/min, of O_2 10 mL/min; 1 Torr = 133.3 Nm^{-2}. CH_4 flow (600–800°C, 5 min) → Ar → O_2 steady flow (600–800°C).

Figures 2 and 3 show profiles of the transient responses to a steady flow of O_2 after CH_x species formed on Ru catalysts at 600, 700, and 800°C, respectively. CH_4 was swept off by Ar before O_2 was introduced. On the Ru/La_2O_3 catalyst, CO was generated immediately when O_2 was introduced, and CO_2 was detected after a slight delay (Fig. 2). Such a delay in CO_2 production might be caused by the adsorption of CO_2 on basic sites of La_2O_3. In contrast, with the Ru/Al_2O_3 catalyst, CO_2 was the major product with only a small amount of CO (Fig. 3). Such differences in the oxidation products on Ru between La_2O_3 and Al_2O_3 seem to be correlated with differences in the catalytic activities of these two catalysts (23). In the oxidation of Ru-CH_x species, CO seems to be produced from highly reactive carbon species. In contrast, less reactive carbon species would be oxidized to give CO_2. Since at a lower temperature the equilibrium between CO and CO_2 shifted to the CO_2 side, at 600°C the

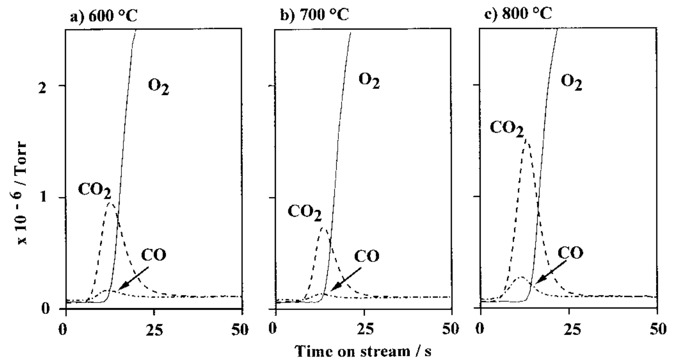

FIG. 3. Transient response of O_2 flow after CH_4 decomposition on Ru/Al_2O_3 at three different temperatures. Reaction conditions: catalyst, Ru (5 wt%)/Al_2O_3 (50 mg); flow rate of CH_4 = 10 mL/min, of O_2 10 mL/min; 1 Torr = 133.3 Nm^{-2}. CH_4 flow (600–800°C, 5 min) → Ar → O_2 steady flow (600–800°C).

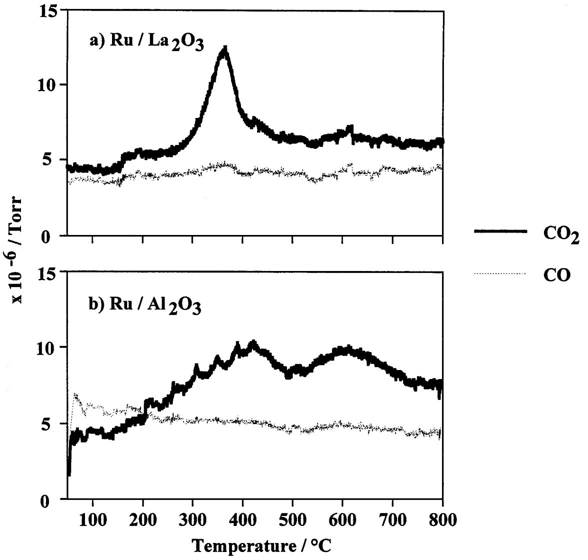

FIG. 4. Temperature-programmed oxidation of surface carbon on the Ru-loaded catalysts. Reaction conditions: reaction temperature of CH_4 on the catalysts: 700°C, catalyst 50 mg; loading level of Ru, 5.0 wt%; flow rate of O_2, 10 mL/min; heating rate, 20°C/min; 1 Torr = 133.3 Nm^{-2}. Decomposition of CH_4 (700°C, 20 min) → Ar → O_2 TPR (10 mL/min).

amount of CO formed from Ru/La_2O_3 was smaller than that of CO_2. Because of the higher background levels of H_2O, the formation of H_2O was not detected.

In the abundant O_2 flow the partial oxidation of CH_x to give CO_2 and H_2O does not readily occur. The most plausible paths are as follows:

$$CH_x + O_2 \rightarrow CO_2 + H_2O \qquad [4]$$

$$CO_2 + C \rightleftarrows 2CO. \qquad [5]$$

To prove the above assumption, temperature-programmed oxidation was carried out. At first, CH_4 was allowed to react with the catalysts at 700°C for 20 min to form CH_x over the catalysts. The catalyst bed temperature was lowered to room temperature under a steady flow of Ar, and temperature-programmed (heating rate, 20°C/min) oxidation was carried out in a neat steady flow of O_2 (Fig. 4).

Over the Ru/La_2O_3 catalyst, a sharp CO_2 response was observed between 300 and 500°C, and the maximum rate of CO_2 formation was observed at 350°C. The trace of CO ($m/z = 28$) was noisy and no significant formation of CO was observed in the range between 100 and 800°C. In contrast, with the Ru/Al_2O_3 catalyst, a broad CO_2 peak was observed between 250 and 800°C. Even at 800°C, unburned carbon species remained. The broad CO_2 response was divided into two broad peaks at 500°C, with the lower temperature response showing its maximum rate at 400°C and the higher temperature response exhibiting its peak at 620°C. A much larger amount of CO_2 was obtained for Ru/Al_2O_3 in the TPO compared to Ru/La_2O_3. However, such differences between the transient response reaction of O_2 and the TPO after the reaction with CH_4 in the amount of CO_2 formed cannot be interpreted at present, since the amounts of H_2 observed during the reaction with CH_4 did not differ significantly. Carbon species on Ru/La_2O_3 seem to be more uniform and reactive, since the oxidation occurs at a lower temperature and in a narrow temperature range. At least two types of carbon species would be formed on Ru/Al_2O_3, with one being reactive and the other less reactive. Neither of them is uniform due to the oxidation occurring in a broad temperature range.

3.3. Temperature-Programmed Reaction with H_2

Figure 5 shows temperature-programmed reductions of CH_x on Ru after the formation of CH_x species at temperatures between 600 and 800°C. As shown in Fig. 5a, over the Ru/La_2O_3 catalyst (reaction of CH_4 at 600°C), the reduction of CH_x to give CH_4 was observed from about 500 to 700°C. This temperature is the lowest temperature at which the CO_2 reforming of CH_4 with Ru catalysts proceeded. In the case of the Ru/Al_2O_3 catalyst, no CH_4 was observed.

The same reaction sequences were carried out with the catalysts at 700 and 800°C to form CH_x from CH_4. Over the Ru/La_2O_3 catalyst, a very large amount of CH_4 formed

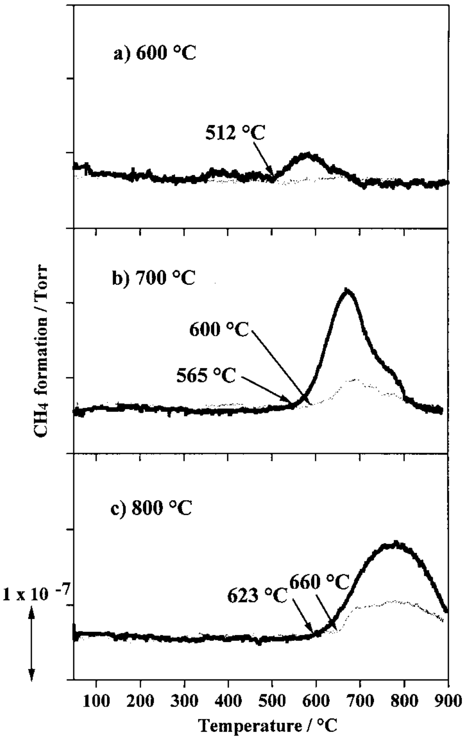

FIG. 5. Temperature-programmed reaction of surface carbon with H_2 on the Ru-loaded catalysts. (—) Ru/La_2O_3; (· · ·) Ru/Al_2O_3, reaction conditions: reaction temperature of CH_4 on the catalysts, 700°C; catalyst 50 mg; loading level of Ru, 5.0 wt%; flow rate of H_2 = 10 mL/min; heating rate, 20°C/min; 1 Torr = 133.3 Nm^{-2}. Decomposition of CH_4 (600–800°C, 20 min) → Ar → H_2 TPR (10 mL/min, 20°C/min).

from 565 to 800°C. In contrast, with the Ru/Al_2O_3 catalyst, the total amount of CH_4 was smaller than that formed with Ru/La_2O_3. The temperature of CH_4 formation in the TPR with H_2 can be classified into three ranges depending on the temperature of the reaction of CH_4 with the catalyst: 500 to 700°C, 600 to 780°C, and 750 to 900°C. Although, as seen in Fig. 1, the amounts of the Ru–CH_x species formed at the same temperature were of the same order of magnitude irrespective of the La_2O_3 or Al_2O_3 support, the reactivity of the CH_x species varied greatly according to the nature of the support. Ru–CH_x species formed at a higher temperature seemed to be less reactive, although the amount of CH_x species was larger than that formed at the lower temperature.

When a La_2O_3 support is chosen for the Ru catalyst showing high activity in the CO_2 reforming of CH_4, it is important to consider the resulting reactivity of the carbon species formed over the Ru metal.

3.4. Temperature-Programmed Reaction with D_2

Temperature-programmed reactions with D_2 were carried out in order to determine the value of x in the CH_x species on the Ru-loaded catalysts (Fig. 6). CH_4 was reacted at 700°C, resulting in the formation of a large amount of CH_4 in the TPR with H_2. Over the Ru/La_2O_3 catalyst, a large amount of CD_4 ($m/z = 20$) was detected at a temperature range of 550 to 800°C, and HD was obtained at temperatures from 100 to 150°C. CH_2D_2, CH_3D, and CHD_3 were not detected. These results indicate that the value of x is almost 0. With the Ru/Al_2O_3 catalyst, CD_4 was again obtained at 600 to 900°C. CH_3D, CH_2D_2, and CHD_3 were not detected. The amount of CD_4 was much smaller than that obtained with Ru/La_2O_3, similar to the results observed in the TPR with H_2. HD was observed in wide temperature ranges between 100 and 150°C and between 150 and 500°C. The formation of HD was observed at a lower temperature in both La_2O_3- and Al_2O_3-loaded cases. The most plausible origin of this species is Ru–H. Judging from the temperature at which the Ru–CH_x species was formed, the formation of a hydride species is suspected. An alternate possible source of the labile hydrogen could be Ru–CH or Ru–CH_3 species, since CHD_3 and CH_3D were not detected in the TPR. Even if Ru–CH or Ru–CH_3 species were formed, they would be transformed into Ru–CD or Ru–CD_3 at a low temperatures. Consequently no CHD_3 or CH_3D was observed.

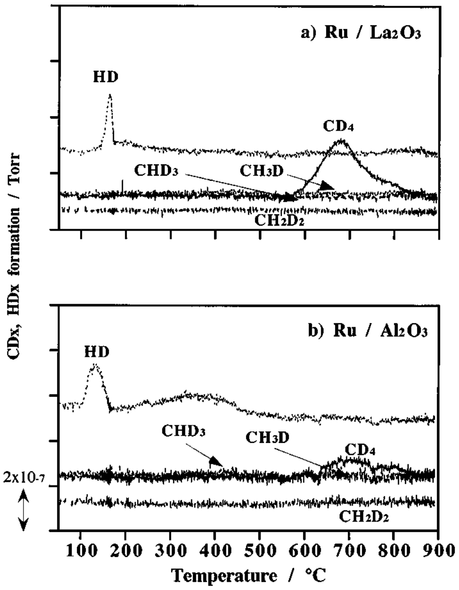

FIG. 6. Temperature-programmed reaction of surface carbon with D_2 on the Ru-loaded catalysts. Reaction conditions: reaction temperature of CH_4 on the catalysts: 700°C, catalyst = 50 mg, loading level of Ru = 5.0 wt%, flow rate: $D_2 = 10$ mL/min, heating rate = 20°C/min, 1 Torr = 133.3 Nm^{-2}. Decomposition of CH_4 (700°C, 20 min) $\rightarrow$ Ar $\rightarrow$ D_2 TPR (10 mL/min, 20°C/min).

Over the Ru/Al_2O_3 catalyst, when an O_2 pulse was introduced at 600°C under a steady flow of Ar after the surface carbon species was removed by the H_2 TPR reaction, the generation of CO_2 was observed. This result indicates that in the case of the Ru/Al_2O_3 catalyst, a certain amount of CH_x species formed on the Ru metal would be very stable and the activation of CH_x with CO_2 or H_2 is very difficult. Mark and Maier reported that the number of H in CH_x species from decomposition of CH_4 over the Rh/Al_2O_3 catalyst was almost nil (27).

The same reaction sequences were carried out on Ru/Y_2O_3 and on Ru/ZrO_2, both of which showed a high level of activity in the CO_2 reforming of methane (Fig. 7) (23). CH_4 was reacted at 700°C. Similar to the results with the Ru/La_2O_3 catalyst, CD_4 was detected in the TPR with D_2. These results indicate that reactive carbon species (Ru–CH_x) were formed over Ru/Y_2O_3 and Ru/ZrO_2. Over Ru/Y_2O_3, between 600 and 750°C, a much larger amount of CD_4 was produced. In addition, very small amounts of CHD_3 and CH_3D were observed at the higher temperature range of 450 to 700°C.

The results of the XRD analyses of the Ru/La_2O_3 catalyst after CO_2 reforming exhibited diffraction peaks assignable to RuO_2 and Ru metal. However, the Ru/Y_2O_3 catalyst showed only diffraction peaks assigned to Ru metal. These results indicate that the decomposition of methane is promoted on Ru metal supported on Y_2O_3.

To determine the value of x in the CH_x species on the Ru/La_2O_3 catalyst (Fig. 8), CD_4 instead of CH_4 was reacted at 700°C to give CD_x species on the Ru/La_2O_3 catalyst. A large amount of CH_4 was formed at a higher temperature range of 500 to 800°C in the TPR with H_2. A very small amount of CH_2D_2 was detected at a low temperature of about 300°C. This phenomenon is closely related to the temperature-programmed reaction with D_2 of surface carbon after CH_4 decomposition (Fig. 6). Due to fragment ions from CD_4 ($m/z = 20$), $CD_2H_2^+$ ($m/z = 18$) and CD_3^+

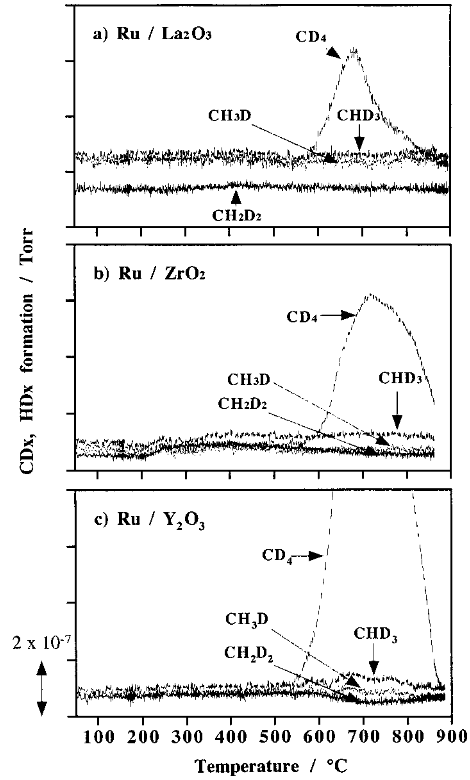

FIG. 7. Temperature-programmed reaction of surface carbon with D_2 on the Ru-loaded catalysts. Reaction conditions: reaction temperature of CH_4 on the catalysts: 700°C, catalyst = 50 mg, loading level of Ru = 5.0 wt%, flow rate: $D_2 = 10$ mL/min, heating rate = 20°C/min, 1 Torr = 133.3 Nm^{-2}. Decomposition of CH_4 (700°C, 20 min) → Ar → D_2 TPR (10 mL/min, 20°C/min).

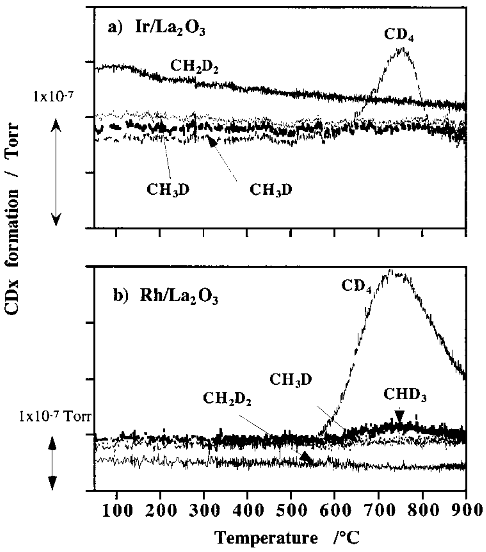

FIG. 9. Temperature-programmed reaction of surface carbon with D_2 on Ir- and Rh-loaded La_2O_3 catalysts. Reaction conditions: reaction temperature: 700°C, catalyst = 50 mg, loading level = 5.0 wt%, flow rate: $D_2 = 10$ mL/min, heating rate = 20°C/min, 1 Torr = 133.3 Nm^{-2}. Decomposition of CH_4 (700°C, 20 min) → Ar → D_2 TPR (10 mL/min, 20°C/min).

($m/z = 18$) cannot be distinguished. If the CD_2 species was formed on Ru as a result of the decomposition of CD_4, TPR with H_2 would produce CD_2H_2 ($m/z = 18$). It therefore can easily be determined that the CD_2 species exists on Ru. The above results indicate that the value of x in CH_x species formed as a result of the decomposition of CH_4 over Ru/La_2O_3 catalysts is almost exclusively 0, with a very small number of species with $x = 2$.

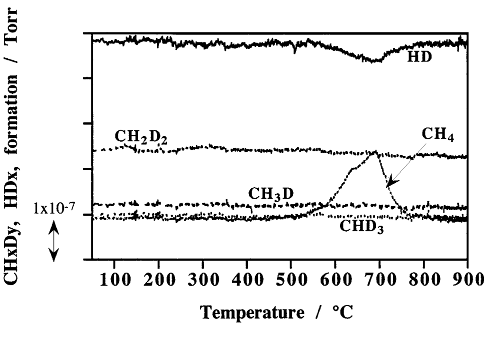

FIG. 8. Temperature-programmed reaction of surface carbon from CD_4 decomposition with H_2 over Ru(5 wt%)/La_2O_3 catalyst. Reaction conditions: decomposition of CD_4: 650°C, 5 mL/min, 20 min, catalyst = 50 mg, flow rate: $H_2 = 10$ mL/min, heating rate = 20°C/min, 1 Torr = 133.3 Nm^{-2}.

The temperature-programmed reaction with D_2 was carried out over Ir/La_2O_3 and Rh/La_2O_3 catalysts in order to compare the differences in noble metals (Fig. 9). In the partial oxidation and CO_2 reforming of methane to synthesis gas, Ir-, Ru-, and Rh-loaded catalysts exhibited high activities (20). As discussed in a previous paper, the partial oxidation of methane on Ir-, Ru-, and Rh-loaded catalysts proceeds by different paths (24, 25). Over the Ir/La_2O_3 catalyst, a small amount of CD_4 ($m/z = 20$) was detected in the temperature range from 600 to 800°C. Such a result is consistent with the fact that the use of an Ir-loaded catalyst does not result in carbon deposition in the partial oxidation and CO_2 reforming of methane (21, 22). The Ir-loaded catalyst exhibited poor activity for the decomposition of methane to CH_x species.

In contrast, Rh/La_2O_3 afforded a much larger amount of CD_4. In addition, a very small amount of CHD_3 was observed at a higher temperature range above 600°C. In the methane decomposition reaction, the Rh/TiO_2 catalyst is reported to produce a large amount of hydrogen with carbon deposition (24), indicating that the Rh metal has a higher level of activity in breaking the C–H bond of CH_4.

Mark *et al.* have reported that there is no detectable effect of the pore structure or the nature of the support on the reaction rate for the CO_2 reforming of CH_4 over Ru, Rh, and Ir catalysts (13). In our studies, however, methane activation on noble metals to give CH_x species depended strongly upon the characteristics of the noble metal species and the support. In most cases, generally the amount of hydrogen in the CH_x species was very small, equal to 2, if hydrogen was present at all, except in the case of Rh loaded on La_2O_3.

4. CONCLUSION

In the Ru-loaded case, the rate of formation of CH_x species in the decomposition of CH_4 and the amount of CH_x species over Ru are independent of the type of support.

The reactivity of Ru-CH_x varies with the decomposition temperature of CH_4. The amount of CH_x species formed on Ru exceeds the stoichiometric amount of Ru. Carbon species on Ru/La_2O_3 seem to be more uniform and reactive than those on Ru/Al_2O_3. CH_x species formed on Ru/Al_2O_3 include less reactive species that do not react with H_2 during TPR at temperatures up to 800°C. The reactivity of CH_x species on Ru depends on the supports, and La_2O_3, Y_2O_3, and ZrO_2 give higher reactivities.

Temperature-programmed reactions with D_2 were carried out in order to determine the value of x for CH_x species on the Ru-loaded catalysts. CD_4 was detected mainly in the TPR with D_2 over Ru-loaded La_2O_3, Y_2O_3, and ZrO_2 catalysts.

The reactivity of CH_x species on Ru and Rh toward D_2 can be divided into two categories. These two species seem not to be based on differences in the value of x in CH_x species. For Ru-loaded La_2O_3, the value of x in CH_x species is nearly equal to 0 with a very small amount of species with $x = 2$. On the other hand, the value of x is almost exclusively 0 in the Rh-loaded case.

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