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Mechanistic study of partial oxidation of methane to synthesis gas over supported rhodium and ruthenium catalysts using in situ time-resolved FTIR spectroscopy

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Abstract

In situ time-resolved FTIR spectroscopy was used to study the reaction mechanism of partial oxidation of methane to synthesis gas and the interaction of $CH_4/O_2/He$ (2/1/45) gas mixture with adsorbed CO species over SiO_2 and γ-Al_2O_3 supported Rh and Ru catalysts at 500–600°C. It was found that CO is the primary product for the reaction of $CH_4/O_2/He$ (2/1/45) gas mixture over H_2 reduced and working state Rh/SiO_2 catalyst. Direct oxidation of methane is the main pathway of synthesis gas formation over Rh/SiO_2 catalyst. CO_2 is the primary product for the reaction of $CH_4/O_2/He$ (2/1/45) gas mixture over Ru/γ-Al_2O_3 and Ru/SiO_2 catalysts. The dominant reaction pathway of CO formation over Ru/γ-Al_2O_3 and Ru/SiO_2 catalysts is via the reforming reactions of CH_4 with CO_2 and H_2O. The effect of space velocity on the partial oxidation of methane over SiO_2 and γ-Al_2O_3 supported Rh and Ru catalysts is consistent with the above mechanisms. It is also found that consecutive oxidation of surface CO species is an important pathway of CO_2 formation during the partial oxidation of methane to synthesis gas over Rh/SiO_2 and Ru/γ-Al_2O_3 catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Partial oxidation of methane; Synthesis gas; Rhodium; Ruthenium; Reaction mechanism; In situ time-resolved FTIR

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1. Introduction

Synthesis gas is the feedstock for large volume process such as methanol and Fischer–Tropsch synthesis [1,2]. The partial oxidation of methane (POM) to synthesis gas is a promising alternative to the conventional stream reforming process due to its mild exothermicity and the more favorable H_2/CO ratio in the gas obtained. A unified mechanism for partial oxidation of methane to synthesis gas over metal catalysts has not been reached so far, especially for the reaction pathway over noble metals. Some people claim that direct oxidation of methane to carbon monoxide and hydrogen (direct route) is the main pathway over supported Ru [3], Rh [4–6], Pd [7] and Pt [8] catalysts. However, other researchers concluded that formation of synthesis gas over the same metals mainly proceeded via the sequential combustion and reforming of methane (indirect route) [9–11]. In the industrial process, if the combustion–reforming mechanism predominantly contributes to the conversion of methane to synthesis gas, severe heat management problems have to be taken into account. Therefore, the elucidation of the reaction pathway is of vital importance.

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In this paper, in situ time-resolved FTIR (in situ TR-FTIR) spectroscopy was used to followed the POM reaction over Rh/SiO_2, Ru/γ-Al_2O_3 and Ru/SiO_2 catalysts, to take aim at contributing to a better understanding of the reaction mechanism over supported noble metal catalysts. The advantage of using TR-FTIR to study the reaction is that both gas phase and surface species formed during the reaction of methane with oxygen can be followed at same time. Therefore, the experiments can provide useful information to the understanding of the reaction pathway. The results of catalytic performance of Rh/SiO_2, Rh/γ-Al_2O_3, Ru/SiO_2 and Ru/γ-Al_2O_3 catalysts for partial oxidation of methane under different space velocity are also presented.

2. Experimental

The supported Rh and Ru catalysts were prepared by the method of incipient wetness impregnation, using metal chloride as the precursor compound for the metal. When the solvent evaporated, the solid material was dried at 110°C and calcined at 500°C for 2 h. The catalyst was then pressed into a self-supporting disk (ca. 10 mg for SiO_2 supported catalyst and ca. 16 mg for γ-Al_2O_3 supported catalyst) for FTIR study. The in situ TR-FTIR experiments were performed using a home-built high temperature in situ IR cell with quartz lining and CaF_2 windows which could be heated from room temperature to 700°C. The schematic diagram of the IR cell is shown in Fig. 1. The internal volume of the IR cell is ca. 25 ml. The gas inlet and outlet of the IR cell were connected to gas line and vacuum system (10^{-3} torr), respectively, through a three-way valve and a two-way valve. By proper switching these valves, the catalyst sample in the IR cell can be evacuated or introduced to different gas atmospheres.

To study the reaction of CH_4/O_2/He (2/1/45, molar ratio) gas mixture over the oxidized or reduced catalyst, the sample in the IR cell was first oxidized with O_2 (99.995%) or reduced with H_2 (99.999%) at 500°C for 60 min followed by evacuation at 500 or 600°C for ∼5 min to remove the gas phase O_2 or H_2. To study the reaction of CH_4/O_2/He gas mixture over the working state catalyst surface, a H_2 reduced catalyst was first pretreated with a gas mixture of CH_4/O_2/He at 500 or 600°C, followed by evacuation to remove the gas phase components. To study the reaction of CH_4/O_2/He gas mixture with adsorbed CO species over the catalyst under the POM reaction condition, the H_2 reduced catalyst was first treated with CH_4/O_2/He gas mixture or ^{13}CO at 500°C to generate adsorbed CO (^{13}CO) species on the catalyst

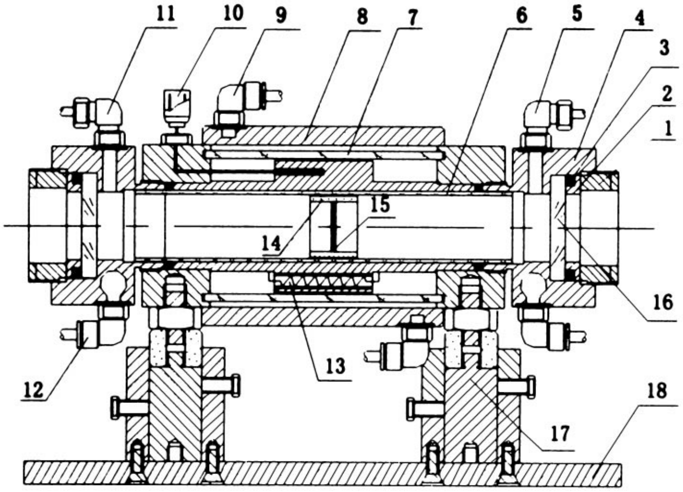

Fig. 1. Schematic diagram of high temperature in situ IR cell. (1) Screw cap; (2) pressing ring; (3) Kalrez O-ring; (4) copper assembly; (5) gas inlet copper fitting; (6) inner quartz tube; (7) outside quartz tube; (8) stainless steel outside sleeve; (9,12) Legris push-in fittings for cooling water; (10) thermal couple; (11) gas outlet copper fitting; (13) heater; (14) sample holder; (15) sample disc; (16) IR window; (17) supporting rod; (18) bottom plate.

surface, followed by briefly evacuation (0.5–1 min) at 500°C to remove the gas phase component. After pretreatment, the catalyst sample under vacuum was carefully switched to a gas mixture of $CH_4/O_2/He$ (∼4 ml, 0.12 MPa) at 500 or 600°C. The equilibrium pressure of the gaseous reactant in the IR cell is about 125 torr. In most TR-FTIR experiments, the gaseous reactant was added to the closed IR cell in a batch mode as described above. In order to get rid of the possible influence of diffusion (mass transfer) effect of the gaseous reactant on the reaction, a comparative TR-FTIR spectroscopy study on the continuous flow reactions of $CH_4/O_2/He$ gas mixture over O_2 and H_2 pretreated catalysts was also performed. In these experiments, the catalyst sample in the IR cell was first oxidized with O_2 or reduced with H_2 at 500°C for 60 min, followed by evacuation at same temperature for ∼5 min to remove the gas phase O_2 or H_2. The IR cell with the pretreated catalyst sample was then filled with 0.10 MPa of N_2 (99.999%) and switched to a flow of $CH_4/O_2/He$ gas mixture (>40 ml/min, 0.10 MPa) at 500°C.

The reaction of $CH_4/O_2/He$ gas mixture over the catalyst was continuously followed with a Perkin Elmer Spectrum 2000 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The IR spectra were recorded at the resolution of 16 cm^{-1} with average of 2–4 scans. The reference spectrum was that of the catalyst prior to the admission of $CH_4/O_2/He$ or ^{13}CO. The time resolution of the spectrum was chosen between 0.28 and 0.6 s, depending on the reaction rate.

Catalytic performance of Rh/SiO_2, $Rh/\gamma\text{-}Al_2O_3$, Ru/SiO_2 and $Ru/\gamma\text{-}Al_2O_3$ catalysts for POM reaction was studied using $CH_4/O_2/Ar = 2/1/45$ (molar ratio) as reaction feed. The catalyst (0.018–0.060 ml) was reduced with H_2 at 600°C for 40 min before it was switched to the reaction feed at 500 or 600°C.

3. Results and discussion

3.1. Interaction of $CH_4/O_2/He$ with oxidized, reduced and working state Rh/SiO_2 catalyst

When an O_2 pretreated 1 wt.%Rh/SiO_2 sample was switched to a gas mixture of $CH_4/O_2/He$ at 500°C, TR-FTIR spectra (Fig. 2) showed that CO_2 (2305, 2350 cm^{-1}) was the first reaction product being observed (0.29 s). The intensities of CO_2 bands increased with increasing of time. Within first 10 s after $CH_4/O_2/He$ was introduced, no IR band of CO species was detected. This observation is consistent with the pulse reaction results over the same catalyst and indicates that fully oxidized rhodium surface is responsible for the formation of CO_2 and H_2O [4]. After about 12 s, IR band of adsorbed CO (2015 cm^{-1}) and those of gas phase CO (2115 and 2172 cm^{-1}) were also detected. Before the appearance of CO adspecies, significant amount of CO_2 has been formed in the IR cell, indicating that part of the Rh atoms have been reduced to metallic state. Over the metallic rhodium sites, two possible reactions leading to the formation of CO should be considered, (I) CH_4 was activated on Rh^0 site and dissociated to surface CH_x ($x = 0$–3) species which was then converted to CO through a series of surface reactions, including the dissociation of H from CH_x and oxidation of surface C species by the oxygen species on the catalyst surface [12]. (II) CH_4 reacted with CO_2 and/or H_2O by reforming reaction to form CO [13]. However, based on the results of TR-FTIR study and catalytic performance evaluation on the reaction of CH_4 with CO_2 over H_2 reduced 1 wt.%Rh/SiO_2 catalyst (see below), it can be concluded that, the reforming of CH_4 with CO_2 was not the dominant reaction pathway to the formation of CO under the experimental condition.

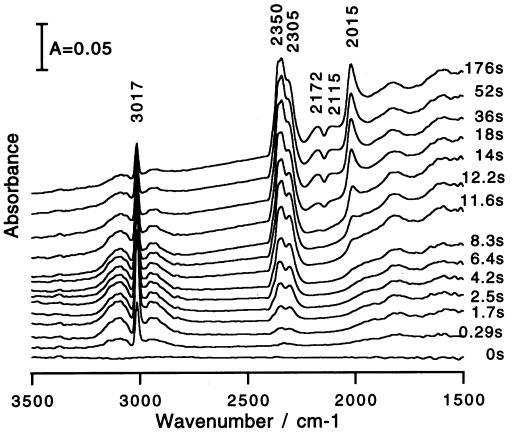

Fig. 2. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture over the O_2 pretreated 1 wt.%Rh/SiO_2 catalyst at 500°C.

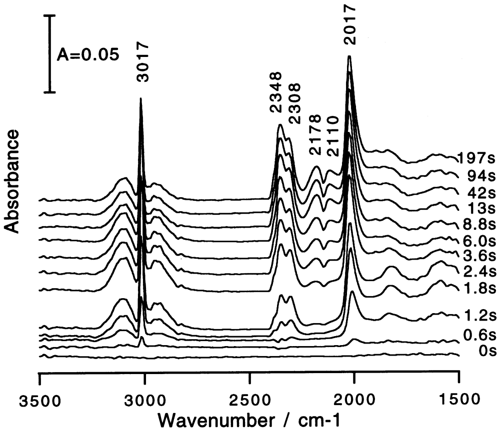

Fig. 3. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture over the H_2 reduced 1 wt.%Rh/SiO_2 catalyst at 500°C.

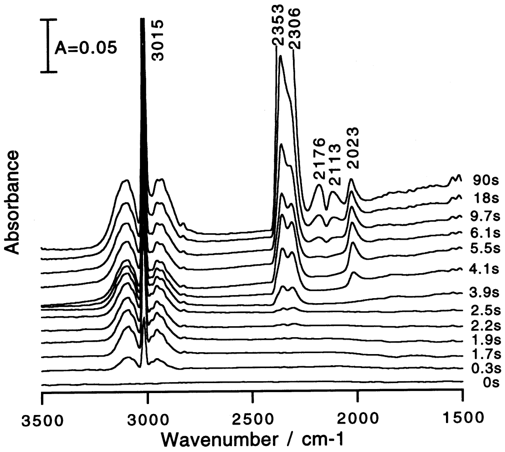

Fig. 4. TR-FTIR spectra of a continuous flow reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture over O_2 pretreated 1 wt.%Rh/SiO_2 catalyst at 500°C. (GHSV $> 140,000\,h^{-1}$).

Different from the situation over the oxidized catalyst, adsorbed CO ($2017\,cm^{-1}$) was the first product being detected (0.6 s) for the reaction of CH_4 and O_2 at 500°C over the H_2 reduced 1 wt.%Rh/SiO_2 catalyst (Fig. 3). The IR bands of CO_2 ($2308, 2348\,cm^{-1}$) and that of gas phase CO ($2110, 2178\,cm^{-1}$) were detected at 1.2 and 1.8 s, respectively, after the catalyst was switched to a gas mixture of $CH_4/O_2/He$. It was also found that, after 3.6 s when $CH_4/O_2/He$ gas mixture was introduced into the IR cell, the IR bands of CH_4 continued to decrease, while those of CO_2 kept increasing. These observations suggested that the reforming reaction may not be a dominant pathway of CO formation under our experimental conditions, otherwise, simultaneous decrease of the IR bands of CH_4 and CO_2 should be observed, especially in the latter period of the reaction.

Figs. 4 and 5 show, respectively, the TR-FTIR spectra when a gas mixture of $CH_4/O_2/He$ continuously flow over the O_2 and H_2 pretreated 1 wt.%Rh/SiO_2 catalysts at 500°C. In these experiments, the gas hourly space velocity (GHSV) of the reactant is higher than $140{,}000\,h^{-1}$. The average contact time of the reactant with the catalyst is, therefore, less than 0.026 s, which is much shorter than the time scale of repeat TR-FTIR measurements (0.3–0.6 s). As it can be seen from Figs. 4 and 5, CO_2 species (1.9–2.2 s) is the primary product for the reaction over O_2 pretreated 1 wt.%Rh/SiO_2, while adsorbed CO species (0.30 s) is the primary product for the reaction over H_2 pretreated sample. These observations are consistent with the results of TR-FTIR experiments shown in Figs. 2 and 3 and indicate that the diffusion (mass transfer) effect of gaseous reactant has no significant influence on the result of TR-FTIR measurement under the experimental conditions, especially in the determination of the primary product of the reaction.

To get rid of the possibility of CO formation through the reforming of CH_4 with CO_2, the

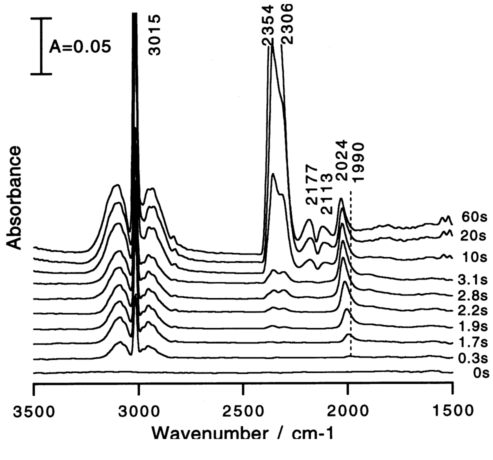

Fig. 5. TR-FTIR spectra of a continuous flow reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture over H_2 reduced 1 wt.%Rh/SiO_2 catalyst at 500°C. (GHSV $> 140,000\,h^{-1}$).

TR-FTIR study on the reaction of CH_4 with CO_2 ($CO_2/CH_4 = 1/1$, 0.30 ml, 0.10 MPa) over a H_2 reduced 1 wt.%Rh/SiO_2 catalyst was also performed. It was found that, compared to the rate of CO formation by direct oxidation of CH_4 (Figs. 3 and 5), the rate of CO formation via the reforming of CH_4 with CO_2 was at least two times slower under the experimental conditions. Therefore, it is very unlikely that the CO formation from the reaction of CH_4/O_2/He gas mixture over the H_2 reduced 1 wt.%Rh/SiO_2 catalyst is via the reforming of CH_4 with CO_2. It must also be realized that, in the early period of POM reaction, the CO_2 concentration over the catalyst is much lower than that used in the TR-FTIR study of the reforming of CH_4 with CO_2. On the other hand, the surface of Rh/SiO_2 catalyst is fully reduced under the reforming conditions, which will offer higher rate for the reaction CH_4 with CO_2. While under the condition of CH_4 partial oxidation, the surface of the catalyst is partially oxidized, on which the rate of reforming reaction will be reduced. Thus, under the POM reaction condition, the difference between the rates of the direct oxidation and reforming reaction may be even larger. Based on the above results, it can be concluded that CO is the primary product of POM reaction over the H_2 reduced Rh/SiO_2 surface.

Fig. 6 shows the TR-FTIR spectra when a CH_4/O_2/He gas mixture pretreated 1 wt.%Rh/SiO_2 sample was switched to a gas mixture of CH_4/O_2/He at 500°C. In general, the evolution of the IR spectra shown in Fig. 6 is quite similar to that observed over the H_2 reduced catalyst discussed above (Figs. 3 and 5). The adsorbed CO (2020 cm^{-1}) species was the first reaction product being observed (0.28 s) on the catalyst. The IR bands of CO_2 (2308, 2350 cm^{-1}) and those of gaseous CO could only be detected after 0.83 and 1.1 s, respectively. These results indicate that CO is also the primary product for the reaction of CH_4/O_2/He gas mixture over the working state Rh/SiO_2 surface.

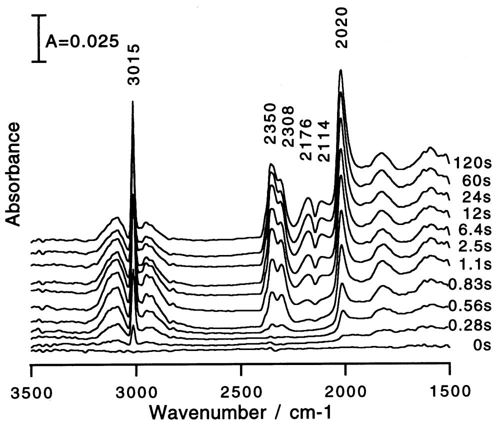

Fig. 6. TR-FTIR spectra of the reaction of CH_4/O_2/He (2/1/45, molar ratio) gas mixture over the working state 1 wt.%Rh/SiO_2 catalyst at 500°C.

The reaction mechanism of partial oxidation of methane over supported rhodium catalysts has been widely studied [4–6,9–11,14]. However, a common opinion on the primary product of the reaction has not been reached so far. Several studies concluded that CO is the primary product of POM reaction over the catalysts [4–6]. In contrast, Baerns and co-workers [10,14] studied the POM reaction over Rh/γ-Al_2O_3 catalyst using TAP reactor and DRIFTS spectroscopy. In the TAP experiment, It was found that CO and CO_2 appeared at the reactor outlet simultaneously during the reaction of methane over Rh/γ-Al_2O_3 catalyst partially reduced by methane, and that the fast reaction of CO_2 was observed only in the presence of carbon deposit. Based on these results, they postulated that CO_2 is the primary product of the reaction and that formation of CO proceeded via a fast reaction between surface carbon species and CO_2. Based on the results of TR-FTIR experiments shown in Figs. 3, 5 and 6, however, the adsorbed CO species was always the first reaction product being observed for the reaction of CH_4/O_2/He gas mixture over H_2 reduced or working state Rh/SiO_2 catalyst surface. Since it took some time for an adsorbed CO species to desorb from the catalyst surface, no IR bands of gaseous CO was detected before the observation of adsorbed CO species. Therefore, the conclusion made on the primary product of POM reaction based simply on the analysis of the appearance of gas phase components in the reaction system may not always be correct. Compared to the CO species, the adsorption of CO_2 on the Rh surface is much weaker under the same condition, as the CO_2 species in the IR cell will be readily removed by evacuation. Moreover, the results of catalytic performance evaluation of the reaction of CO_2/CH_4 (1/1, molar ratio) gas mixture over H_2 reduced 1 wt.%Rh/SiO_2 indicated that the

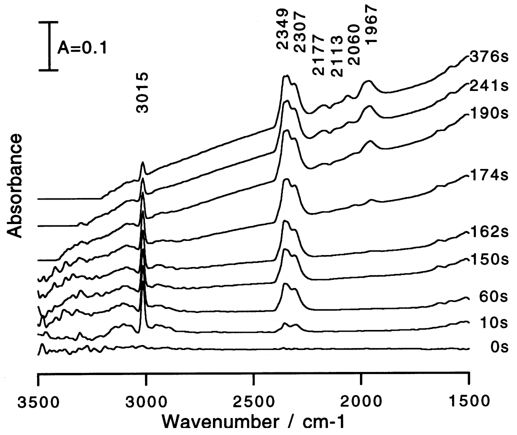

Fig. 7. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture over O_2 pretreated 2 wt.%Ru/γ-Al_2O_3 catalyst at 500°C.

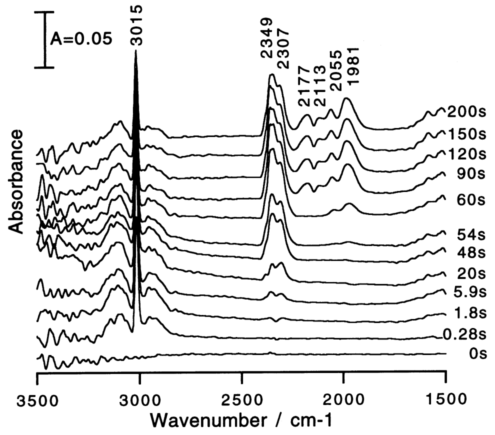

Fig. 8. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture over H_2 reduced 2 wt.%Ru/γ-Al_2O_3 catalyst at 500°C.

conversions of CO_2 and CH_4 were less than 5% at 500°C with GHSV $= 54,000\,h^{-1}$. Corresponding TR-FTIR study on the reaction of CH_4 with CO_2 at 500°C over H_2 reduced 1 wt.%Rh/SiO_2 also indicated that the IR band of adsorbed CO can only be detected after ca. 1.2–2.5 s, which is slower than the rate of CO formation (~0.3 s) through the direct oxidation of CH_4 (Figs. 3 and 5). So it is unlikely that the dominant pathway of CO formation for the POM reaction over Rh/SiO_2 catalyst is via the reaction of CO_2 with surface carbon species. A possible explanation for the fast formation of CO_2 in Bearn and co-workers' experiment is that the consecutive oxidation of surface CO species takes place at a very fast rate under the experimental conditions. A detailed TR-FTIR study on the reaction of $CH_4/O_2/He$ gas mixture with adsorbed CO species over the catalyst will be presented in the following section of this paper.

3.2. *Interaction of* $CH_4/O_2/He$ *with oxidized, reduced and working state* Ru/γ-Al_2O_3 *catalyst*

Exposure of $CH_4/O_2/He$ to an O_2 pretreated 2 wt.%Ru/γ-Al_2O_3 at 500°C led to the observation of CO_2 (2307, 2349 cm^{-1}) as the primary reaction product (Fig. 7). With the increase of time, IR band of gas phase CH_4 (3015 cm^{-1}) continued to decrease, while the bands of CO_2 increased only in first 190 s period, and remained almost unchanged in rest time of reaction. IR band of adsorbed CO (1967, 2060 cm^{-1}) and those of gas phase CO (2115, 2177 cm^{-1}) was detected after 162 and 174 s, respectively. Similar phenomenon was observed for the reaction of $CH_4/O_2/He$ over H_2 reduced sample (Fig. 8). But in the later case, since the catalyst has been reduced with H_2 before it was switched to the reactant, the bands of adsorbed CO (1981, 2055 cm^{-1}) appeared much earlier than the former one. Fig. 9 shows the TR-FTIR spectra when a $CH_4/O_2/He$ gas mixture pretreated 2 wt.%Ru/γ-Al_2O_3 sample was switched

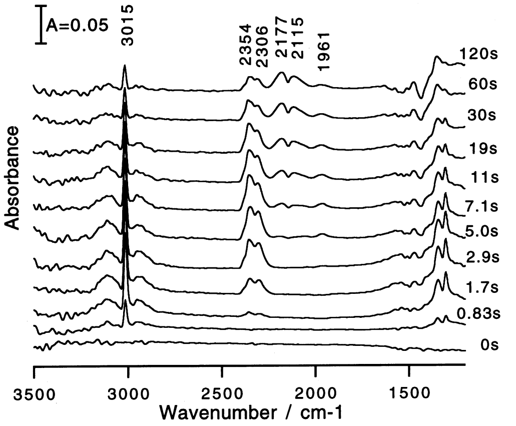

Fig. 9. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture over the working state 2 wt.%Ru/γ-Al_2O_3 catalyst at 600°C.

to $CH_4/O_2/He$ at 600°C. As it can be seen, IR bands of CO_2 were observed at 1.7 s, and their intensities rapidly increased within first 5 s period. The band of adsorbed CO (1961 cm^{-1}) and those of gas phase CO (2115, 2177 cm^{-1}) were detected at 5.0 and 7.1 s, respectively. After 7.1 s, both of the IR bands for CH_4 and CO_2 decreased with time, while the bands of gaseous CO continued to increase. These experiments clearly indicate that CO_2 is the primary product of POM reaction over Ru/γ-Al_2O_3 catalyst and that partial oxidation of methane to synthesis gas over the catalyst is proceeded by combustion–reforming mechanism. This conclusion is also consistent with the mechanism proposed by Guerrero-Ruiz and co-workers for the POM reaction over Ru/γ-Al_2O_3 and Ru/SiO_2 catalysts based on results of isotopic tracing experiment [9].

3.3. *Interaction of* $CH_4/O_2/He$ *with* Ru/SiO_2 *catalyst*

The POM reaction over the H_2 reduced 2 wt.%Ru/SiO_2 catalyst is also studied at 500 and 600°C using TR-FTIR. Compared to the Ru/γ-Al_2O_3 catalyst, the reaction over Ru/SiO_2 catalyst proceeds at much slower rate. At 600°C, CO_2 was the only reaction product being observed within first 20 min period. After this point, gaseous CO was also found. However, no IR band of adsorbed CO was detected. This result suggested that combustion–reforming mechanism is also the dominant pathway of CO formation for the POM reaction over Ru/SiO_2 catalyst. One possible reason for the low activity of Ru/SiO_2 is attributable to a low surface area of Ru [15]. However, it was also found that the nature of support also induced notable difference in the catalysts related to the capacity of decomposition of CH_4 [15,16]. It has been reported that alumina is a support that a higher dehydrogenation ability confers to metal, followed by titania, silica, and finally, by magnesia [16].

3.4. *Interaction of* $CH_4/O_2/He$ *with adsorbed* CO *species over* Rh/SiO_2 *and* Ru/γ-Al_2O_3 *surfaces*

To elucidate the reaction pathway of CO_2 formation through CO oxidation under POM condition, the interaction of $CH_4/O_2/He$ gas mixture with adsorbed CO species over the 1 wt.%Rh/SiO_2 and 2 wt.%Ru/γ-Al_2O_3 catalysts was studied by TR-FTIR spectroscopy at 500°C. Before the introducing of $CH_4/O_2/He$ gas mixture, the H_2 reduced Rh/SiO_2 and Ru/γ-Al_2O_3 samples were pretreated with $CH_4/O_2/He$ at 500°C, followed by brief evacuation (0.5–1 min) at same temperature to remove just the gas phase components but leave the adsorbed CO species on the catalysts. On both catalysts, CO_2 is formed shortly after the pretreated catalysts were switched to $CH_4/O_2/He$. However, over Rh/SiO_2 (Fig. 10), no decrease in the intensity of IR band of surface CO (2017 cm^{-1}) species was observed, while over Ru/γ-Al_2O_3 (Fig. 11), the formation of CO_2 (2310, 2350 cm^{-1}) was accompanied by rapid consumption of surface CO species (1983, 2057 cm^{-1}). The experiment using ^{13}CO as tracing molecule showed that (Fig. 12), when a Rh/SiO_2 catalyst with pre-adsorbed ^{13}CO was switched to a gas mixture of $CH_4/O_2/He$, the surface ^{13}CO species was quickly oxidized to $^{13}CO_2$. However, since CO is the primary product of POM reaction over Rh/SiO_2 catalyst, the reacted ^{13}CO adspecies will be rapidly replenished by the adsorbed ^{12}CO species, which is formed by direct oxidation of CH_4. These observations indicate that consecutive oxidation of surface CO species is an important pathway of CO_2 formation for the POM reaction over Rh/SiO_2 and Ru/γ-Al_2O_3 catalysts. The results also provide further experimental evidences for the different mechanisms of partial oxidation of methane to synthesis gas over Rh/SiO_2 and Ru/γ-Al_2O_3 catalysts.

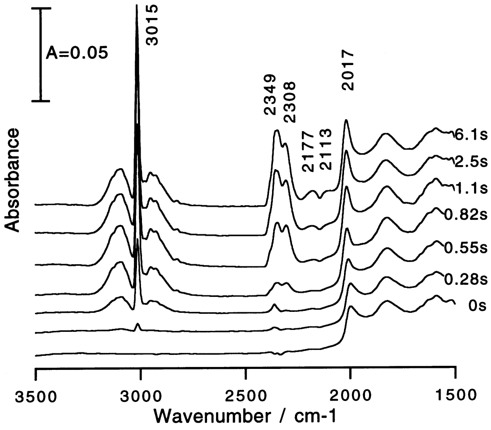

Fig. 10. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture with adsorbed CO species over 1 wt.%Rh/SiO_2 catalyst with at 500°C.

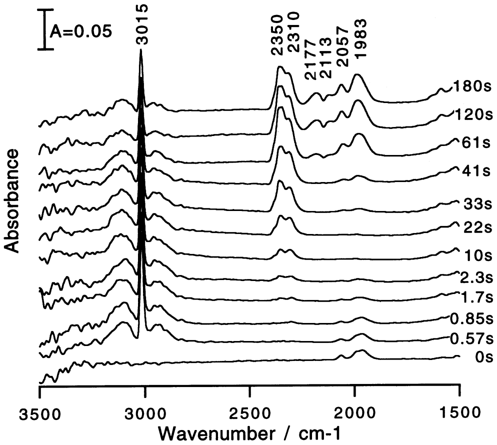

Fig. 11. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture with adsorbed CO species over 2 wt.%Ru/γ-Al_2O_3 catalyst at 500°C.

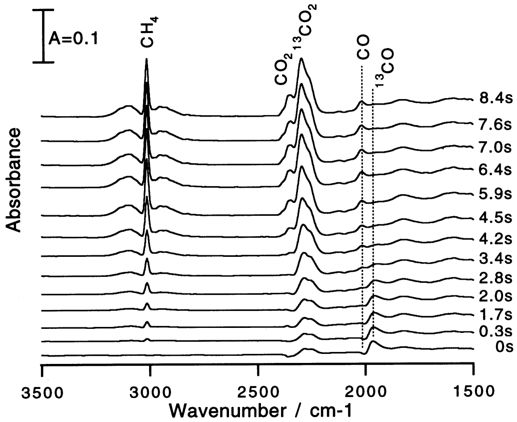

Fig. 12. TR-FTIR spectra of the reaction of $CH_4/O_2/He$ (2/1/45, molar ratio) gas mixture with adsorbed ^{13}CO species over 1 wt.%Rh/SiO_2 catalyst at 500°C.

3.5. *Effect of space velocity on the partial oxidation of methane over* SiO_2 *and* γ-Al_2O_3 *supported* Rh *and* Ru *catalysts*

In order to obtain more information on the reaction pathway of synthesis gas production over Rh/SiO_2, Rh/γ-Al_2O_3, Ru/SiO_2 and Ru/γ-Al_2O_3 catalysts, the influence of gas hourly space velocity (GHSV) of the reactant on the catalytic performance of POM reaction over the supported Rh and Ru catalysts were studied at 500 and 600°C, respectively (Table 1). For the SiO_2 and γ-Al_2O_3 supported Rh catalysts, when the GHSV increased from 54,000 to 216,000 h^{-1}, the selectivities to H_2 and CO_2 decreased, while the selectivity to CO increased. With further increasing of GHSV from 216,000 to 360,000 h^{-1}, the selectivities on 1 wt.%Rh/SiO_2 catalyst is almost unchanged, while the selectivity of CO_2 on 1 wt.%Rh/γ-Al_2O_3 continues to decrease and that of CO continues to increase. Over both catalysts, the variation of GHSV has only little effect on the conversion of CH_4. For the SiO_2 and γ-Al_2O_3 supported Ru catalysts, however, the conversion of methane and the selectivity of CO decreased, while the selectivity of CO_2 increased with increasing GHSV.

Table 1
Catalytic performance of SiO_2 and γ-Al_2O_3 supported Rh and Ru catalysts for partial oxidation of methane[a]

Catalyst	Temperature (°C)	GHSV (h^{-1})	CH_4 conversion (%)	Selectivity (%)			H_2/CO
				CO	H_2	CO_2	
1 wt.%Rh/SiO_2	500	54000	55.4	62.6	86.3	37.4	2.76
		216000	55.8	72.3	76.4	27.7	2.11
		360000	53.4	71.5	75.1	28.5	2.10
1 wt.%Rh/γ-Al_2O_3	500	54000	47.5	47.7	83.7	52.3	3.51
		216000	46.0	55.0	78.1	45.0	2.84
		360000	47.6	60.4	77.2	39.6	2.55
4 wt.%Ru/SiO_2	600	54000	83.9	90.9	89.6	9.1	1.97
		216000	79.1	88.4	88.8	11.6	2.01
		360000	77.3	87.0	87.3	13.0	2.01
4 wt.%Ru/γ-Al_2O_3	600	54000	83.6	89.3	89.3	10.7	2.00
		216000	73.6	85.6	88.2	14.4	2.06

[a] Feed: $CH_4/O_2/Ar = 2/1/45$ (molar ratio); data were obtained after 15 min on stream.

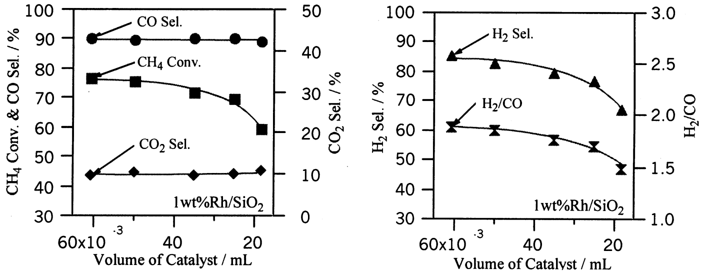

Fig. 13. Influence of catalyst volume on the POM performance of 1 wt.%Rh/SiO$_2$ catalyst at 600°C. Feed: CH$_4$/O$_2$/Ar = 2/1/45 (molar ratio). Data were obtained after 30 min on stream.

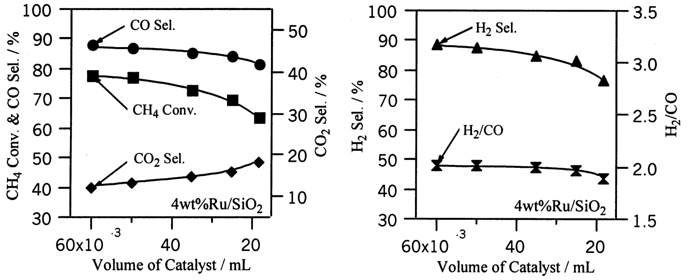

Fig. 14. Influence of catalyst volume on the POM performance of 4 wt.%Ru/SiO$_2$ catalyst at 600°C. Feed: CH$_4$/O$_2$/Ar = 2/1/45 (molar ratio). Data were obtained after 30 min on stream.

In another experiment, the flow rate of the reactant was remained at 300 ml/min. The variation of GHSV was achieved by changing the volume of catalysts. It was found that, when the volume of catalyst was reduced from 0.06 to 0.018 ml (Figs. 13 and 14), the CO selectivity over 1 wt.%Rh/SiO$_2$ catalyst remained almost unchanged, while that over 4 wt.%Ru/SiO$_2$ catalyst gradually decreased from 88.1 to 81.7%, although the conversion of CH$_4$ over both catalysts decreased significantly. All of these results are in support of the mechanisms proposed based on the TR-FTIR studies for the POM reaction over SiO$_2$ and γ-Al$_2$O$_3$ supported Rh and Ru catalysts. The significant difference in the reaction mechanisms of partial oxidation of methane to synthesis gas over supported Rh and Ru catalysts may be ascribed to the higher affinity for oxygen on Ru compared to Rh. The results of in situ microprobe Raman spectroscopic characterization indicated that, during the simultaneous interaction of CH$_4$/O$_2$/Ar gas mixture with 4 wt.%Rh/SiO$_2$ and 4 wt.%Ru/SiO$_2$ catalysts, no Raman band of rhodium oxide (491 cm^{-1}) was detected over the Rh/SiO$_2$ catalyst at 500°C. Over the Ru/SiO$_2$, however, Raman bands attributable to ruthenium oxide (489, 609 cm^{-1}) can even be detected at 600°C. These observations suggest that Ru/SiO$_2$ catalyst has a much higher tendency to be oxidized than Rh/SiO$_2$ catalyst. Therefore, the significant difference in the mechanisms of POM reaction over the supported Rh and Ru catalysts may have resulted from the difference in the concentration of surface of oxygen species (O^{2-}) over two catalyst systems under the reaction conditions.

4. Conclusions

Based on the results of TR-FTIR study and the catalytic performance evaluation over Rh/SiO$_2$, Rh/γ-Al$_2$O$_3$, Ru/SiO$_2$ and Ru/γ-Al$_2$O$_3$ catalysts, following conclusions can be made:

1. CO is the primary product of POM reaction over the H$_2$ reduced and working state Rh/SiO$_2$ catalyst. Direct oxidation of CH$_4$ to synthesis gas is the main pathway of POM reaction over Rh/SiO$_2$

catalyst. Compared to the direct oxidation of CH_4 to CO, the reforming of CH_4 with CO_2 is not the dominant route of CO formation over the catalyst.
2. CO_2 is the primary product of POM reaction over Ru/γ-Al_2O_3 and Ru/SiO_2 catalysts. The dominant reaction pathway for CO formation over Ru/γ-Al_2O_3 catalyst is via the reforming reactions of CH_4 with CO_2 and H_2O. Significant difference in the mechanisms of partial oxidation of methane over the supported Rh and Ru catalysts may have resulted from the difference in the concentration of surface of oxygen species (O^{2-}) over two catalyst systems under the reaction conditions.
3. For the POM reaction over Rh/SiO_2 and Ru/γ-Al_2O_3 catalysts, consecutive oxidation of surface CO species is an important pathway of CO_2 formation.

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