The concentration of oxygen species over SiO_2-supported Rh and Ru catalysts and its relationship with the mechanism of partial oxidation of methane to synthesis gas

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The partial oxidation of methane (POM) to synthesis gas over SiO_2-supported Rh and Ru catalysts was studied by *in situ* microprobe Raman and *in situ* time-resolved FTIR (TR-FTIR) spectroscopies. The results of *in situ* microprobe Raman spectroscopic characterization indicated that no Raman band of Rh_2O_3 was detected at 500 °C over the Rh/SiO_2 catalyst under a flow of a $CH_4/O_2/Ar$ (2/1/45, molar ratio) mixture, while the Raman bands of RuO_2 can even be detected at 600°C over the Ru/SiO_2 catalyst under the same atmosphere. The experiments of *in situ* TR-FTIR spectroscopic characterizations on the reactions of CH_4 over O_2 pre-treated Rh/SiO_2 and Ru/SiO_2 catalysts indicated that the products of CH_4 oxidation over Rh/SiO_2 and Ru/SiO_2 greatly depend on the concentration of O^{2-} species over the catalysts. On the catalysts with high concentration of O^{2-}, CH_4 will be completely oxidized to CO_2. However, if the concentration of O^{2-} species over the catalysts is low enough, CH_4 can be selectively converted to CO without the formation of CO_2. The parallel experiments using *in situ* TR-FTIR spectroscopy to monitor the reaction of the $CH_4/O_2/Ar$ (2/1/45, molar ratio) mixture over Rh/SiO_2 and Ru/SiO_2 catalysts show that the mechanisms of synthesis gas formation over the two catalysts are quite different. On the Rh/SiO_2 catalyst, synthesis gas is mainly formed by the direct oxidation of CH_4, while on the Ru/SiO_2 catalyst, the dominant pathway of synthesis gas formation is *via* the sequence of total oxidation of CH_4 followed by reforming of unconverted CH_4 with CO_2 and H_2O. The significant difference in the mechanisms of partial oxidation of CH_4 to synthesis gas over Rh/SiO_2 and Ru/SiO_2 catalysts can be well related to the difference in the concentration of O^{2-} species over the catalysts under the reaction conditions mainly due to the difference in oxygen affinity of the two metals.

KEY WORDS: partial oxidation of methane; synthesis gas; reaction mechanism; rhodium; ruthenium; *in situ* microprobe Raman; *in situ* time-resolved FTIR

1. Introduction

The mechanism of partial oxidation of methane (POM) to synthesis gas over noble metal catalysts is still under debate [1–6]. Two reaction schemes have been suggested in the literature. Marin and co-workers [1,2], based on the results of TAP study on the POM and related reactions over Pt and Rh sponge, concluded that synthesis gas was produced as the primary products over the catalysts and the reaction between surface carbon atom and oxygen present as platinum or rhodium oxide resulted in the formation of carbon monoxide. Mirodatos and co-workers [3] studied the POM reaction over platinum gauze using a high temperature TAP-2 reactor and concluded that carbon monoxide and hydrogen could be produced directly from the methane and solid oxidized platinum. In contrast to the direct oxidation mechanism, Buyevskaya *et al.* [4–6] studied the interaction of CH_4 and CH_4/O_2 mixtures with rhodium black and Rh/ γ-Al_2O_3 using a TAP reactor and *in situ* DRIFT spectroscopy and concluded that the primary steps of partial oxidation of methane over rhodium catalysts included methane dissociation to give a surface CH_x ($x = 1$–3) species and the total oxidation of CH_x to CO_2 and H_2O. The CO and H_2 are produced by the reactions of surface CH_x with CO_2 or H_2O(OH).

The nature of the oxygen species and their specific role in the mechanism of partial oxidation of methane are also unclear. Marin and co-workers [1,2] believe the oxygen present as platinum or rhodium oxide results in the formation of carbon monoxide. Both metal oxides and chemisorbed oxygen species are involved in the consecutive oxidation of carbon monoxide and hydrogen. The dissolved oxygen species in the platinum catalyst is responsible for the oxidation of methane to carbon dioxide and water. Mirodatos and coworkers [3] found that product distribution for the POM reaction over platinum gauze was determined by the surface oxygen concentration. In the absence of gas phase O_2, the diffusion of oxygen from the platinum bulk toward the surface is slower than the desorption of carbon monoxide and hydrogen and synthesis gas is produced with high selectivity. In the presence of gas phase oxygen, the surface oxygen concentration is very high and the consecutive oxidation of carbon monoxide and hydrogen takes place. Au and Wang [7], however, suggested that chemisorbed oxygen species are involved in the oxidation of methane.

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In order to obtain a better understanding of the nature of the oxygen species over the real POM catalyst under the reaction conditions, a study on the surface of the Rh/SiO_2 and Ru/SiO_2 catalysts at 500–600 °C under O_2, H_2/Ar (5/95, molar ratio) and $CH_4/O_2/Ar$ (2/1/45, molar ratio) atmosphere was carried out using *in situ* microprobe Raman spectroscopy. Parallel experiments using *in situ* time-resolved FTIR (TR-FTIR) spectroscopy to follow the reaction of CH_4 over Rh/SiO_2 and Ru/SiO_2 with different surface oxygen concentration and the POM reaction over H_2-reduced catalysts were also performed. It is expected that these experiments can provide more information to the understanding of nature of the oxygen species and their specific role in the POM reaction.

2. Experimental

The Rh/SiO_2 and Ru/SiO_2 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 experiments of *in situ* microprobe Raman spectroscopic characterization of the catalysts were performed using a home-built high temperature *in situ* microprobe Raman cell, which allows us to record the Raman spectra of the catalyst from room temperature to 700 °C under different gas atmosphere. The Raman spectrum was recorded on a Dilor LabRam I confocal microprobe Raman system. The exciting wavelength was 632.8 nm from Ar^+ laser with power of 10 mW and a spot of *ca.* 3 μm on the catalyst surface. The laser beam was focused on the top of the catalyst bed. In each experiment, the catalyst (*ca.* 2.5×10^{-3} ml) was first treated in a flow of O_2 (99.995%) at 500 °C for 30 min. After O_2 pretreatment, the Raman spectra of the catalyst were recorded at each specified temperature point under a flow of O_2. The catalyst was then switched to a flow of H_2/Ar (5/95, molar ratio) at 500 or 600 °C to take the Raman spectra of the H_2-reduced sample. Finally, the H_2-reduced sample was switched to a flow of simulated POM feed ($CH_4/O_2/Ar = 2/1/45$, molar ratio) to take the Raman spectra of the catalyst at 500 or 600 °C under POM conditions. In all Raman experiments, the flow rate of the gas (O_2, H_2/Ar or $CH_4/O_2/Ar$) is higher than 5 ml/min.

The *in situ* time-resolved FTIR experiments were performed on a Perkin–Elmer spectrum 2000 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a home-built high temperature *in situ* IR cell with quartz lining and CaF_2 windows [8]. The catalyst was pressed to a self-supporting disk (~10 mg). To study the reaction of CH_4 over the catalysts with different surface oxygen concentration, the catalyst was first oxidized with O_2 (99.995%) at 600 °C for 1 h followed by evacuation (10^{-3} Torr) at 500 °C for different periods of time to remove gas phase O_2 and part of the surface oxygen species. The treated catalyst was then switched to 0.12 ml (0.10 MPa) of CH_4 at 500 or 600 °C. To study the POM reaction over the catalyst, the catalyst was first reduced with H_2 (99.999%) at 600 °C in the IR cell for 60 min followed by evacuation at 500 or 600 °C for *ca.* 5 min to remove the gas phase H_2. After evacuation, the IR cell was filled with 0.10 MPa of Ar (99.999%) and then switched to a flow of simulated POM feed ($CH_4/O_2/Ar = 2/1/45$, molar ratio) at 500 or 600 °C. The flow rate of the feed is higher than 68 ml/min. The IR spectra of the surface and the gas phase species formed during the reaction were continuously recorded at a resolution of 16 cm^{-1} with average of two scans. The time interval between two recorded spectra was less than 0.3 s. The reference spectrum was that of the catalyst prior to the admission of CH_4 or $CH_4/O_2/Ar$ mixture.

3. Results and discussion

3.1. *In situ microprobe Raman spectroscopy characterization on the Rh/SiO_2 and Ru/SiO_2 catalysts under O_2, H_2/Ar (5/95) and $CH_4/O_2/Ar$ (2/1/45) atmosphere*

Figure 1 (a) and (b) show the Raman spectra of the 4 wt% Rh/SiO_2 catalyst recorded at 500 and 600 °C, respectively, under a flow of O_2. A broad band with maximum at *ca.* 491 cm^{-1} is observed. This band can be assigned to rhodium oxide (Rh_2O_3) [9]. It was reported that, under O_2 atmosphere, a complete oxidation of Rh to Rh_2O_3 took place at temperature above 500 °C [10]. When the

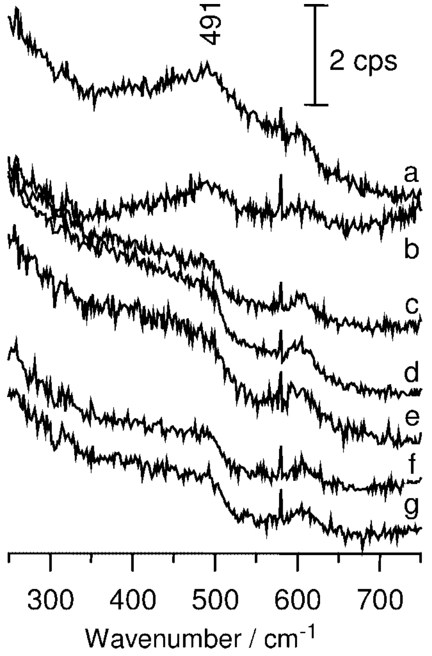

Figure 1. *In situ* microprobe Raman spectra of 4 wt% Rh/SiO_2 catalyst: (a) in a flow of O_2 at 500 °C, (b) heating to 600 °C in a flow of O_2 after (a), (c) switching to a flow of H_2/Ar (5/95) mixture at 600 °C after (b), (d) cooling to 500 °C in a flow of H_2/Ar (5/95) mixture after (c), (e) switching to a flow of $CH_4/O_2/Ar$ (2/1/45) mixture at 500 °C after (d), (f) heating to 600 °C in a flow of $CH_4/O_2/Ar$ (2/1/45) mixture after (e) and (g) reacting at 600 °C in a flow of $CH_4/O_2/Ar$ (2/1/45) mixture for 20 min.

O_2-pre-treated 4 wt% Rh/SiO_2 sample was switched to a flow of H_2/Ar at 600 °C, the band of Rh_2O_3 species disappeared (figure 1(c)). A similar spectrum was observed when the catalyst was cooled to 500 °C under the same atmosphere (figure 1(d)). After reducing with H_2/Ar mixture at 500 °C for 30 min, the catalyst was switched to a flow of simulated POM feed ($CH_4/O_2/Ar = 2/1/45$, molar ratio) at 500 °C and the corresponding Raman spectrum is shown in figure 1(e). It is interesting to see that the Raman spectrum of the catalyst recorded under a simulated POM feed is very similar to that of the catalyst recorded under H_2/Ar atmosphere. No Raman band of Rh_2O_3 species was detected (figure 1(e)). A similar spectrum was obtained when the catalyst was heated in a flow of $CH_4/O_2/Ar$ mixture from 500 to 600 °C (figure 1(f) and (g)). This experimental finding clearly indicated that most of the surface Rh species in the catalyst bed are in the metallic state under the conditions of partial oxidation of methane. The same conclusion was drawn by Marin and co-workers [1] based on the results of a TAP experiment. It was found that, by assuming an oxide stoichiometric of Rh_2O_3, only 0.4 wt% of Rh_2O_3 is present during the simultaneous interaction of CH_4 and O_2 at a stoichiometric feed ratio with the rhodium sponge.

Figure 2 (a) and (b) are the Raman spectra of the 4 wt% Ru/SiO_2 catalyst recorded at 500 and 600 °C, respectively, under a flow of O_2. Two bands attributable to ruthenium oxide (RuO_2) were observed at 489 and 609 cm^{-1} [11, 12]. These bands vanished when the O_2-pre-treated 4 wt% Ru/SiO_2 was switched to a flow of H_2/Ar at 600 °C (figure 2(c)), and were found to reappear when the H_2/Ar-pre-treated 4 wt% Ru/SiO_2 catalyst was switched to a flow of $CH_4/O_2/Ar$ mixture at the same temperature (figure 2 (d) and (e)). Obviously, the surface of the Ru/SiO_2 catalyst contained a considerably larger amount of oxygen species (O^{2-}) than that of the Rh/SiO_2 catalyst under the POM reaction conditions, indicating that the former catalyst has a much higher tendency to be oxidized, as compared to the latter one. A possible reason for this may be the higher oxygen affinity of ruthenium compared with that of rhodium. On both 4 wt% Rh/SiO_2 and 4 wt% Ru/SiO_2 catalysts, no Raman band of surface dioxygen species such as O_2^{2-} and O_2^- was detected under O_2 and $CH_4/O_2/Ar$ atmosphere.

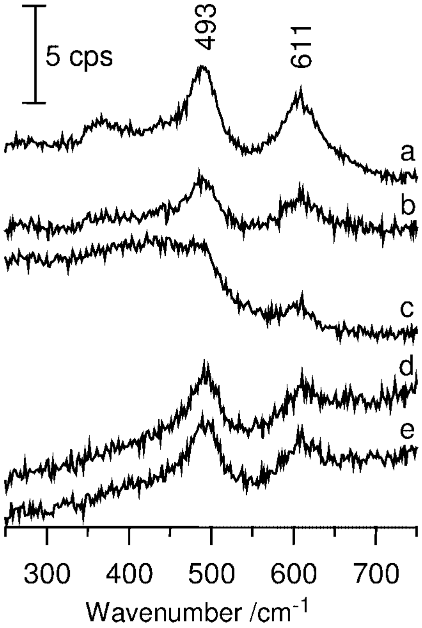

Figure 2. *In situ* microprobe Raman spectra of 4 wt% Ru/SiO_2 catalyst: (a) in a flow of O_2 at 500 °C, (b) heating to 600 °C in a flow of O_2 after (a), (c) switching to a flow of H_2/Ar (5/95) mixture at 600 °C after (b), (d) switching to a flow of $CH_4/O_2/Ar$ (2/1/45) mixture at 600 °C after (c) and (e) reacting at 600 °C in a flow of $CH_4/O_2/Ar$ (2/1/45) mixture for 20 min.

In order to elucidate the relationship between the concentration of oxygen species over supported Rh and Ru catalysts and the mechanisms of POM reaction, parallel experiments using *in situ* TR-FTIR spectroscopy to monitor the reaction of CH_4 over the 1 wt% Rh/SiO_2 and 4 wt% Ru/SiO_2 catalysts with different surface oxygen concentration was performed.

3.2. *In situ time-resolved FTIR spectroscopy study on the reaction of CH_4 over Rh/SiO_2 and Ru/SiO_2 catalysts with different surface oxygen concentration*

Heating an oxidized Rh/SiO_2 catalyst at 500 °C under vacuum will result in gradual reduction of the sample. The Rh/SiO_2 catalysts with different surface oxygen concentration can therefore be prepared by evacuating fully oxidized catalyst samples at elevated temperature for different periods of time.

Figure 3 shows the TR-FTIR spectra recorded at 500 °C for the reaction of CH_4 (0.12 ml, 0.10 MPa) over a 1 wt% Rh/SiO_2 catalyst which had been oxidized with O_2 at 600 °C

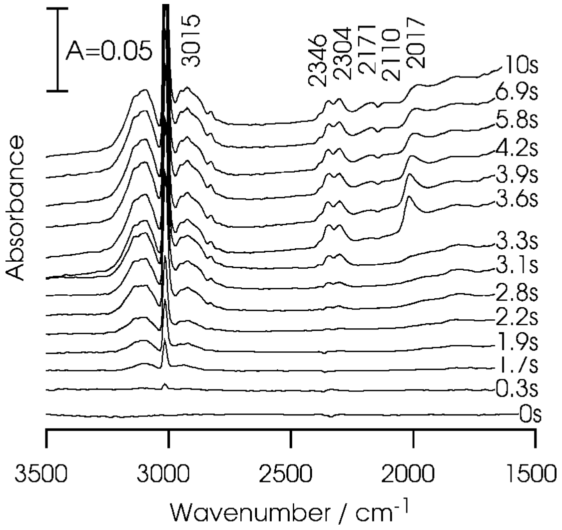

Figure 3. *In situ* TR-FTIR spectra of the reaction of CH_4 (0.12 ml, 0.10 MPa) over 1 wt% Rh/SiO_2 catalyst at 500 °C. Before the admission of CH_4, the catalyst was first oxidized with O_2 at 600 °C for 1 h followed by evacuation at 500 °C for 2–3 min.

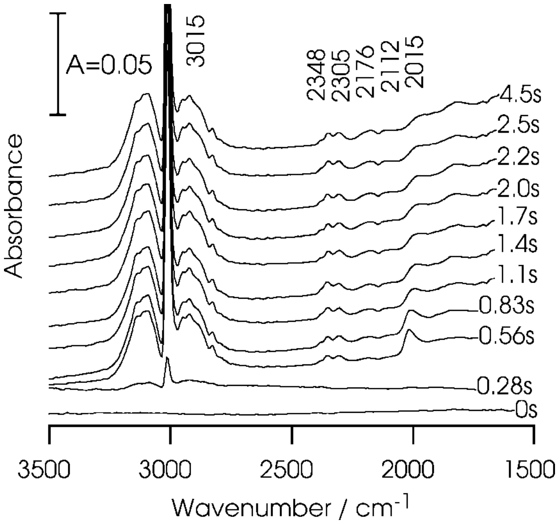

Figure 4. *In situ* TR-FTIR spectra of the reaction of CH_4 (0.12 ml, 0.10 MPa) over 1 wt% Rh/SiO_2 catalyst at 500 °C. Before the admission of CH_4, the catalyst was first oxidized with O_2 at 600 °C for 1 h followed by evacuation at 500 °C for 15 min.

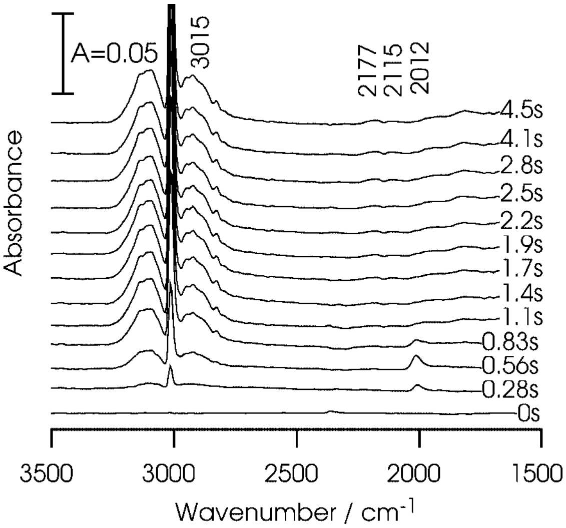

Figure 5. *In situ* TR-FTIR spectra of the reaction of CH_4 (0.12 ml, 0.10 MPa) over 1 wt% Rh/SiO_2 catalyst at 500 °C. Before the admission of CH_4, the catalyst was first oxidized with O_2 at 600 °C for 1 h followed by evacuation at 500 °C for 30 min.

for 1 h followed by evacuation at 500 °C for 2–3 min. In this experiment, since the O_2-pre-treated Rh/SiO_2 catalyst was only evacuated at 500 °C for a very short period of time, the oxygen concentration over the catalyst is pretty high. As can be seen from figure 3, CO_2 (2304 and 2346 cm^{-1}) is the first reaction product observed (2.2 s). The intensity of CO_2 bands increased with increasing time. Within the first 3 s after CH_4 was introduced, no IR band of CO species was detected. These results are consistent with the results reported by Baerns and co-workers [5] based on the TAP experiments, and indicated that the oxidized rhodium catalyst is responsible for the formation of CO_2. Accompanied by the formation of CO_2, the baseline of the spectra changed significantly, indicating that the catalyst was reduced by CH_4. After *ca.* 3.3 s, the IR band of adsorbed CO (2017 cm^{-1}) [6] and those of gaseous CO (2110 and 2171 cm^{-1}) were detected. Over the reduced Rh site, two possible reactions can lead to the formation of CO. One is the reforming of unconverted CH_4 with CO_2 and H_2O. The other is the direct oxidation of CH_4 to CO without the experience of CO_2 and H_2O as reaction intermediates. However, according to our previous *in situ* TR-FTIR study on the POM and related reactions over the Rh/SiO_2 catalyst, the reforming reaction is not the dominant pathway for the CO formation over the catalyst [8]. Further experimental evidence on the reaction mechanism will be given in the following section of this paper.

Figure 4 shows the TR-FTIR spectra recorded at 500 °C for the reaction of CH_4 (0.12 ml, 0.10 MPa) over a 1 wt% Rh/SiO_2 catalyst which had been oxidized with O_2 at 600 °C for 1 h followed by evacuation at 500 °C for 15 min. In this experiment, since the oxidized Rh/SiO_2 sample had been evacuated at 500 °C for 15 min, the initial concentration of oxygen species over the catalyst was lower than in the case shown in figure 3. As can be seen from figure 4, both IR bands of CO_2 (2305 and 2348 cm^{-1}), adsorbed CO (2015 cm^{-1}) and gas phase CO (2112 and 2176 cm^{-1}) species were detected at the same time shortly after CH_4 was introduced. If the initial concentration of oxygen species over the catalyst was further reduced by evacuating a fully oxidized catalyst at 500 °C for 30 min, the reaction of CH_4 will lead to the formation of CO species only (figure 5). Marin and co-workers [1] studied the interaction of O_2 with rhodium sponge using a TAP reactor and found that, in addition to Rh_2O_3, oxygen is also present in the form of a chemisorbed species which is believed to be involved in the nonselective reaction paths of the partial oxidation of methane. It was also found that the chemisorbed oxygen species will be completely desorbed after 2 s under vacuum [1]. Based on these results and the results of our corresponding Raman experiments shown in figure 1, it is reasonable to conclude that the oxygen species involved in the *in situ* TR-FTIR experiments shown in figures 3–5 is O^{2-}. The above TR-FTIR experiments clearly indicate that the O^{2-} species over the Rh/SiO_2 is responsible for both partial (to CO) and complete (to CO_2) oxidation of CH_4. The products of CH_4 oxidation greatly depend on the concentration of O^{2-} species over the catalyst.

Unlike the Rh/SiO_2 catalyst, evacuating a fully oxidized Ru/SiO_2 catalyst at 600 °C resulted in no significant reduction of the sample, as evidenced by the fact that no detectable change in the baseline of the IR spectra of the catalyst was observed during the evacuation. Figure 6 shows the TR-FTIR spectra recorded at 500 °C for the reaction of CH_4 (0.12 ml, 0.10 MPa) over a 4 wt% Ru/SiO_2 catalyst which has been oxidized with O_2 at 600 °C for 1 h followed by evacuation at the same temperature for 1 h. Similar to the reaction of CH_4 over the oxidized 1 wt% Rh/SiO_2, CO_2 (2302

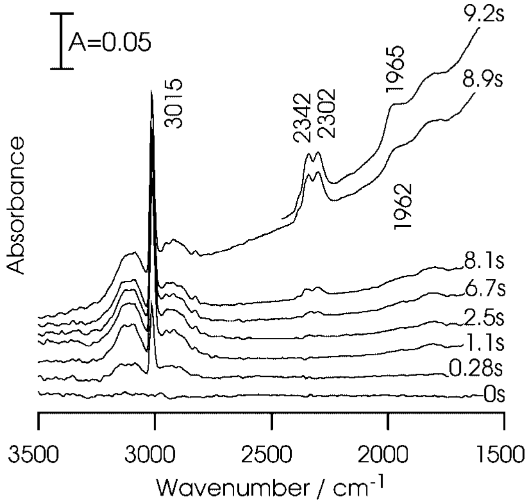

Figure 6. *In situ* TR-FTIR spectra of the reaction of CH_4 (0.12 ml, 0.10 MPa) over 4 wt% Ru/SiO_2 catalyst at 500 °C. Before the admission of CH_4, the catalyst was first oxidized with O_2 at 600 °C for 1 h followed by evacuation at same temperature for 1 h.

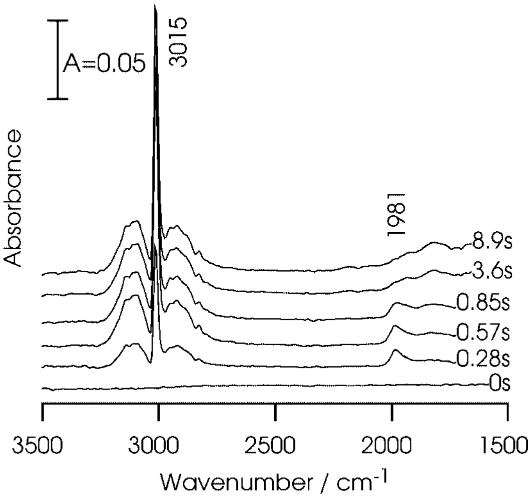

Figure 7. *In situ* TR-FTIR spectra of the reaction of CH_4 (0.12 ml, 0.10 MPa) over 4 wt% Ru/SiO_2 catalyst at 500 °C. Before the admission of CH_4, a fully oxidized 4 wt% Ru/SiO_2 catalyst was first reacted with CH_4 (0.12 ml, 0.10 MPa) at 500 °C for 2 min (to remove part of the O^{2-} species over the catalyst) followed by evacuation at same temperature for 10 min.

and 2342 cm^{-1}) is the only reaction product being detected within the first 8 s after CH_4 is introduced. The IR band of adsorbed CO species (1962 cm^{-1}) [13] is detected when a significant amount of ruthenium oxide is reduced (8.9 s), as evidenced by the observation of a significant change in the baseline of the IR spectra recorded after 8.9 s. If CH_4 was introduced to a 4 wt% Ru/SiO_2 catalyst which had been fully oxidized with O_2 at 600 °C followed by treating with a certain amount of CH_4 (0.12 ml, 0.10 MPa) at 500 °C to remove part of the O^{2-} species over the catalyst, the only reaction product detected by the IR spectrometer is CO (figure 7). The above results indicate that the oxidation products of CH_4 on the O_2-pre-treated Ru/SiO_2 are also determined by the concentration of O^{2-} species over the catalyst.

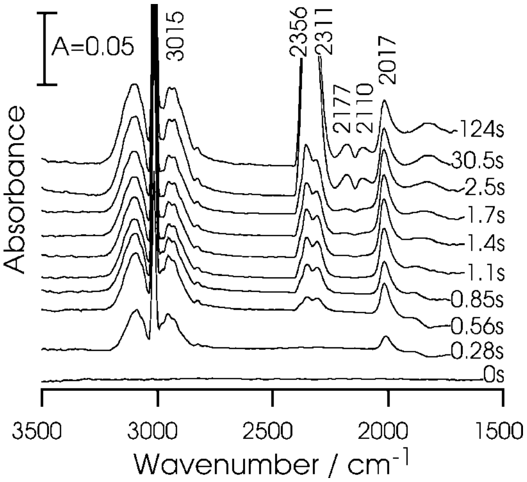

Figure 8. *In situ* TR-FTIR spectra of a flow reaction of $CH_4/O_2/Ar$ (2/1/45) mixture over H_2-reduced 1 wt% Rh/SiO_2 at 500 °C.

3.3. *In situ time-resolved FTIR spectroscopy study on the reaction of the $CH_4/O_2/Ar$ mixture over H_2-reduced Rh/SiO_2 and Ru/SiO_2 catalysts*

In order to elucidate the relationship between the concentration of O^{2-} over the Rh/SiO_2 and Ru/SiO_2 catalysts under the POM reaction conditions and the reaction schemes for partial oxidation of methane to synthesis gas, the reactions of a simulated POM feed with $CH_4/O_2/Ar = 2/1/45$ over H_2-reduced 1 wt% Rh/SiO_2 and 1 wt% Ru/SiO_2 catalysts were followed by *in situ* TR-FTIR spectroscopy.

The TR-FTIR spectroscopic investigation on the reaction of the $CH_4/O_2/Ar$ gas mixture over the H_2-reduced 1 wt% Rh/SiO_2 catalyst was performed at 500 °C. The corresponding IR spectra are shown in figure 8. It was found that, when a H_2-reduced 1 wt% Rh/SiO_2 was switched to a flow of $CH_4/O_2/Ar$ gas mixture (GHSV $> 180\,000$ h^{-1}) at 500 °C, the adsorbed CO species with IR band at 2017 cm^{-1} was the first reaction product observed (0.28 s). The IR bands of CO_2 (2311 and 2356 cm^{-1}) and gas phase CO (2110 and 2177 cm^{-1}) were detected at 0.56 and 1.1 s, respectively. Since no CO_2 species were observed in the spectrum recorded at 0.28 s, it is very unlikely that the adsorbed CO species detected at this stage is from the CO_2 reforming of CH_4 unless the rate of CH_4 reforming with CO_2 is higher than the rate of CH_4 combustion. The result of catalytic performance evaluation on the reaction of a CH_4/CO_2 (1/1, molar ratio) mixture over a H_2-reduced 1 wt% Rh/SiO_2 catalyst indicated that, at 500 °C with GHSV $= 54\,000$ h^{-1}, the conversions of CH_4 and CO_2 were less than 5%, which is much lower than the conversion of CH_4 in the partial oxidation reaction. At higher GHSV, the contribution of CH_4/CO_2 reforming to the CO formation will be even lower. It should also be realized that the surface of the Rh/SiO_2 catalyst is fully reduced under the reforming conditions, which will be favorable to the reaction of CH_4 with CO_2. While under the condition of CH_4 partial oxidation, the surface of the catalyst is at least partially oxidized, on which the rate of reforming reaction will be reduced. Based on these results and analysis,

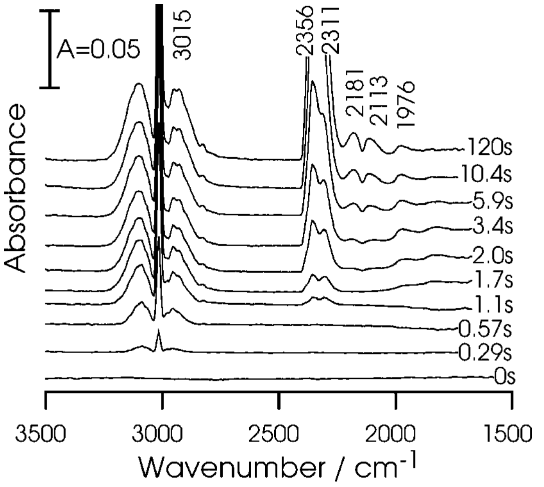

Figure 9. *In situ* TR-FTIR spectra of a flow reaction of $CH_4/O_2/Ar$ (2/1/45) mixture over H_2-reduced 1 wt% Ru/SiO_2 at 600 °C.

it is reasonable to conclude that the adsorbed CO species detected at 0.28 s in the IR spectrum shown in figure 8 is from the direct partial oxidation of CH_4.

Different from the situation over the 1 wt% Rh/SiO_2 catalyst, the reaction of the $CH_4/O_2/Ar$ gas mixture (GHSV $>$ 180 000 h^{-1}) over a H_2-reduced 1 wt% Ru/SiO_2 catalyst at 600 °C led to the formation of CO_2 (2311 and 2356 cm^{-1}) as the primary product (figure 9). IR bands of adsorbed CO (1976 cm^{-1}) and those of gaseous CO (2113 and 2181 cm^{-1}) were detected at 2.0 s. This result clearly indicates that CO_2 is the primary product of POM reaction over the Ru/SiO_2 catalyst and the mechanism of partial oxidation of methane to synthesis gas over the catalyst is *via* combustion of CH_4 to CO_2 and H_2O followed by reforming of unconverted CH_4 with CO_2 and H_2O. These results are also consistent with the conclusion drawn by Guerrero-Ruiz *et al.* [14] and Verykios and co-workers [15] for the POM reaction over Ru/Al_2O_3 and Ru/SiO_2 catalysts based on results of isotopic tracing experiments.

According to the results of *in situ* microprobe Raman experiments shown in figures 1 and 2, the significant difference in the mechanisms of partial oxidation of CH_4 synthesis gas over Rh/SiO_2 and Ru/SiO_2 catalysts can be well related to the difference in concentration of O^{2-} over the catalysts under the reaction conditions. For the SiO_2-supported Rh catalyst, even when the laser beam of the spectrometer was focused on the top of the catalyst bed, no Raman band of Rh_2O_3 species was detected on a working catalyst. This indicated that most of the surface Rh species in the catalyst bed are in the metallic state under the condition of partial oxidation of methane. On the Rh^0 sites, CH_4 can be activated by dissociation to a surface CH_x ($x = 0$–3) species which is then converted to CO through a series of surface reactions [16], including the dissociation of H from CH_x and oxidation of surface C species by the oxygen species (*e.g.*, O^{2-}) on the catalyst surface. For the SiO_2-supported Ru catalyst, however, the Ru species near the top of the catalyst bed is almost fully oxidized under POM reaction conditions.

According to the results of the TR-FTIR experiment shown in figure 6, such kind of Ru species will predominantly catalyze complete oxidation of CH_4 to CO_2 and H_2O. Over the Ru/SiO_2 catalyst, if the flow rate of the feed is not very high, oxygen in the CH_4/O_2 mixture will be completely consumed in a narrow zone near the front of the catalyst bed. The Ru species at the rear of the catalyst bed will remain in metallic state, which will catalyze the reforming reactions of the resulting $CH_4/CO_2/H_2O$ mixture to synthesis gas.

4. Conclusions

Based on the above *in situ* microprobe Raman and *in situ* TR-FTIR spectroscopic characterizations on the POM and related reactions over SiO_2-supported Rh and Ru catalysts, it can be concluded that the products of CH_4 oxidation over Rh/SiO_2 and Ru/SiO_2 are determined by the concentration of O^{2-} species over the catalysts. On the catalysts with high concentration of O^{2-}, CH_4 will be completely oxidized to CO_2. However, if the concentration of O^{2-} over the catalysts is low enough, CH_4 can be selectively oxidized to CO without the formation of CO_2. The mechanisms of POM reaction over the two catalysts are quite different. Direct oxidation of CH_4 to synthesis gas is the main pathway of POM reaction over the Rh/SiO_2 catalyst, while the combustion-reforming mechanism is the dominant pathway of synthesis gas formation over Ru/SiO_2 catalysts. The significant difference in the reaction schemes of POM reaction over Rh/SiO_2 and Ru/SiO_2 catalysts can be well related to the difference in the surface concentration of O^{2-} species over the catalysts under the reaction conditions mainly due to the difference in oxygen affinity of the two metals.

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