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Partial oxidation of methane to syngas over Rh/SiO_2 catalyst using on-line MS

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Abstract

The partial oxidation of methane to syngas (POM) over a Rh/SiO_2 catalyst was investigated by temperature program desorption (TPD), temperature program reduction (TPR), temperature program surface reaction (TPSR), and temperature program reaction. Interaction of CH_4/Ar or CH_4/O_2/Ar with Rh/SiO_2 catalyst was examined by pulse and transient reaction techniques. The experiment results showed that the POM over Rh/SiO_2 catalyst is through a dissociation-oxidizing mechanism. Methane dissociates to surface species, such as CH_x ($x = 1$–3) and adsorbed atomic hydrogen on the catalyst, then the surface CH_x ($x = 1$–3) species combine with the surface active oxygen species to generate CO and H_2. CO_2 could come from further oxidation of CH_x, CO, and other carbon species.

Keywords: Methane; Partial oxidation; Syngas; Rh/SiO_2 catalyst; MS

1. Introduction

The partial oxidation of methane to syngas (POM) has been extensively studied in recent years [1–5]. This reaction is a potential process for syngas production. There are enormous efforts contributed to catalyst performance and fundamental investigations. However, some aspects concerning both application and fundamental issues of POM are still under disputation [6–10]. Therefore, there is still work to do in both fundamental and practice.

Au and Wang [11] compared the activity and selectivity of methane dissociate-activation and oxidation towards syngas on SiO_2 supported Ni and Cu catalysts by pulsing reaction technique. It was found that the generation of CO and H_2 differs from the thermolysis-oxidizing mechanism that Hickman and Schmidt [12] suggested. Au et al. also pointed out that the dissociation of methane is the key step in the reaction. Marin and coworkers [13] studied POM over a supported Pt catalyst by pulsing reaction and TAP. They found that CO is the primary product, while CO_2 is the deep oxidation product of CO. Ruckenstein and Hu [14] studied POM on the supported metal catalyst by pulsing reaction. They came to the same conclusion as that gotten by Marin et al. that CO is generated before CO_2. They thought that the generation of CO and H_2 fellows the mechanism that Schmidt et al. suggested. Baerns and coworkers [15] studied POM on a Rh/γ-Al_2O_3 catalyst by transient pulse technique. They thought that CO is generated from the reaction of CO_2 with surface carbon species. Wang et al. [16] examined the POM reaction by isotope pulsing reaction by using CH_4/O_2 and CD_4/O_2 as reactants and discovered the isotopic effect of deuterium. Based on the two-step reaction mechanism of POM. Dissanayake et al. [17] suggested that NiO and Ni^0 species on catalyst are the active sites for methane complete oxidation and reforming reaction, respectively. Buyevskaya and coworkers [15,18] suggested that Rh^0 and Rh–O are the active sites for methane dissociating to hydrocarbon species, carbon, and the oxidation of these carbon containing species. They also showed that there is rapid reaction between surface carbon and CO_2 to form CO. Mallens et al. [13] studied the activity of dissolved oxygen and surface oxygen on the platinum oxide,

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and found that the Pt oxide is the active site for POM. Dissanayake et al. [19] reported that the catalyst bed has a temperature gradient higher than 300 °C (hot spots) during POM under the condition of high space velocities. In order to avoid the "hot spots" problem and to investigate easily, Wang et al. [20] studied the interaction between CH_4 and Rh catalyst, or CH_4:O_2 (2:1) and Rh catalyst by pulse reaction, the result indicated that Rh is the active center for POM.

Based on the previous work, there are still work need to be done concerning on the fundamental aspects for partial oxidation of methane to syngas over Rh/SiO_2 catalyst. The activation of methane on Rh/SiO_2 catalyst was studied by temperature program reduction (TPR), temperature program desorption (TPD), temperature program surface reaction (TPSR), and on-line mass spectrometry.

2. Experiments

2.1. Catalyst preparation

The catalyst was prepared by impregnation. The support SiO_2 (60–80 mesh) was impregnated with the methanol solution of $RhCl_3$, dried at 110 °C for 12 h, calcined at 500 °C for 6 h to obtain the final catalyst.

2.2. Temperature program experiments

The temperature program experiments include temperature program reduction (TPR), temperature program desorption (TPD), H_2-temperature program surface reaction (H_2-TPSR), temperature program reaction. All the experiments were carried out in a quartz tubular fixed-bed reactor (3 mm ID, 18 cm in length). In the reaction, 50 mg catalyst was used. An on-line Balzers quadruple mass spectrometer (QMS200) was employed to continuously monitor the effluent from the reactor. The effluent contains H_2, He, CH_4, H_2O, CO or N_2 ($m/z = 28$), O_2, and CO_2.

2.2.1. Temperature program reaction

The temperature program reaction on oxidized catalyst Rh (O)/SiO_2 is carried at following conditions. The catalyst was heated to 700 °C in O_2 atmosphere, and maintained for 10 min, then cooled to room temperature and switched to He to purge for 30 min. After introducing CH_4/O_2 until the base line is straight, the temperature-program reaction was carried out with a heat-

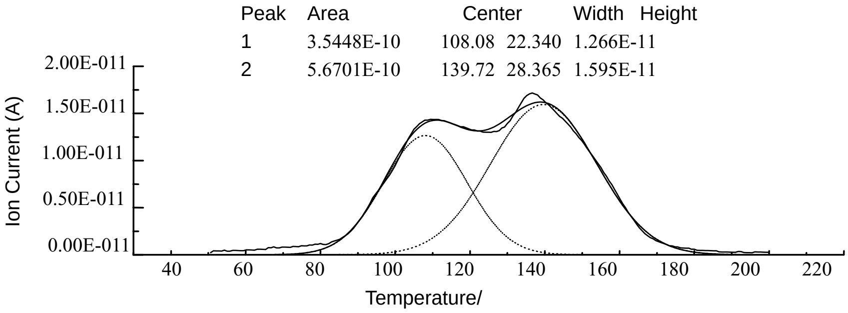

Fig. 1. TPR profile of 1 wt.% Rh/SiO_2 catalyst.

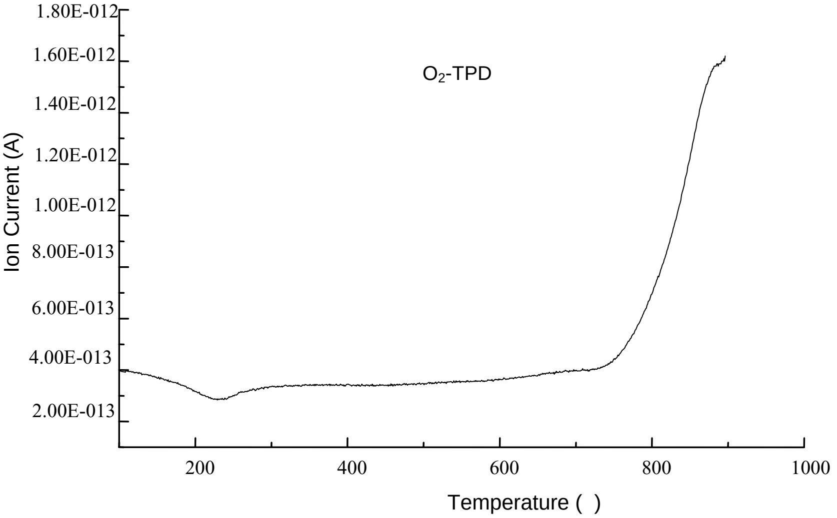

Fig. 2. O_2-TPD profile of 1 wt.% Rh/SiO_2 catalyst.

ing rate of 10 °C/min. For the temperature program reaction on the reduced catalyst Rh/SiO$_2$, the catalyst was heated to 700 °C under a H$_2$–N$_2$ mixture and kept at this condition for 10 min, then cooled to room temperature and switched to He to purge for 30 min. After introducing CH$_4$/O$_2$ and waiting until the base line is straight, the temperature-program reaction was carried out with a heating rate of 10 °C/min.

2.2.2. The temperature program reduction (TPR)

Catalyst (100 mg) was used for the experiment. The catalyst was pre-heated to 700 °C from room temperature in oxygen, and then cooled to room temperature in oxygen. The H$_2$/N$_2$ mixture (containing 3.0 mol% H$_2$) was switched to the reactor to purge the system for 30 min, and then the temperature program reduction was carried out with a heating rate of 25 °C/min.

2.2.3. Oxygen temperature program desorption (TPD)

The catalyst was primarily heated to 700 °C in O$_2$, kept at this temperature for 20 min, then cooled to room temperature in O$_2$, and then switched to He purging for 30 min. After the base line was stabilized, the temperature program desorption was carried out with a heating rate of 25 °C/min up to 1000 °C, while helium was used as carry gas.

2.2.4. The temperature program surface reaction (H$_2$-TPSR)

The catalyst had been reduced in H$_2$ at 700 °C for 30 min, and purged by helium for 30 min, and then CH$_4$/He or CH$_4$/O$_2$/He mixture was admitted into reactor. After reacting for 1 min by using (CH$_4$/He) or 10 min by using (CH$_4$/O$_2$/He) at 700 °C, helium was used to purge the reactor (for 30 min), and the reactor was cooled to room temperature in helium. The temperature program reduction was carried out by using H$_2$/N$_2$ (containing 3 mol% H$_2$) as reactant. The heating rate is 25 °C/min.

2.3. Pulse reactions and transient reactions

The pulse reaction was carried out in a fixed bed reactor with 50 mg catalyst. The catalyst was primarily heated and purged in O$_2$ stream at 700 °C to remove organic contaminates. After cooling to room temperature, H$_2$/N$_2$ (3 mol% H$_2$) mixture was used as reactant to carry out reaction. Temperature was raised to 700 °C in H$_2$/N$_2$ mixture, and then helium was used to purge the catalyst (for 20 min). The pulse volume was 1.0 mL in the reaction. The reactants and products were brought out by helium flow and analyzed on an on-line mass spectroscopy (Balzers Ominster QMS200).

The transient response experiments were carried out at 500 and 700 °C and 1 atm. The reactants were CH$_4$/O$_2$/Ar (2/1/20 in volume) or CH$_4$/Ar (1/10 in volume).

3. Results and discussion

3.1. The temperature program reduction (TPR) of Rh/SiO$_2$

Fig. 1 shows the TPR profile of 1.0 wt.% Rh/SiO$_2$ catalyst prepared by impregnation. The reduction reaction occurs in the temperature range of 80–180 °C. There are two reduction peaks at $T_m = 108$ and 140 °C with area ratio of $A_{108}/A_{140} = 3.5/5.7$. Hence, there are types of Rhodium oxides. Since rhodium has oxidation state +I, +II, and +III, and stable oxide Rh$_2$O$_3$, there might be Rh$_2$O, RhO, and Rh$_2$O$_3$ on the catalyst surface. The different reduction temperatures shown in Fig. 1 might come from different surface rhodium species. Rh$_2$O$_3$ species on surface is relatively easier to be reduced comparing to Rh$_2$O and RhO. Hence, the reduction peak at 108 °C might be generated from the reduction of Rh$_2$O$_3$ species, while the reduction peak at 140 °C might be the reduction of Rh$_2$O and RhO.

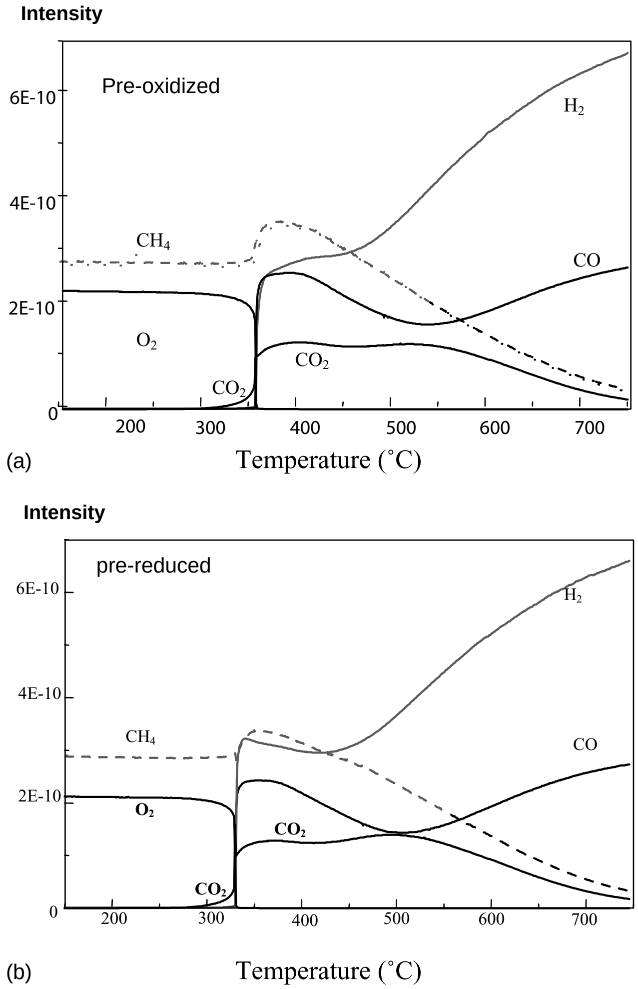

Fig. 3. Temperature programmed reaction profile on 1 wt.% Rh/SiO$_2$ catalyst: (a) the pre-oxidized Rh (O); (b) the pre-reduced Rh/SiO$_2$ catalyst.

3.2. Temperature program desorption (TPD) of Rh (O)/SiO_2

Fig. 2 shows the O_2-TPD over 1.0 wt.% Rh/SiO_2 catalyst. Very small amount of oxygen desorbs below 750 °C, most of the oxygen desorbs above 750 °C. It indicates that the rhodium oxide species start to decompose to metal rhodium and oxygen at this temperature above 750 °C. In the rhodium decomposition process, highly oxidative oxygen species such as [O] might be generated. The newly generated [O] can oxidize methane. These results consistent with that the POM reaction is usually carried out at temperature above 700 °C.

3.3. Temperature program reaction

Fig. 3a shows the ionic intensity of reactants and products during POM reaction. With temperature increases over oxidized Rh/SiO_2 catalyst, the reaction starts at 310 °C to generate CO_2. The major product is CO_2 from 310 to 350 °C. There is a suddenly reaction light up temperature point at 350 °C. It indicates that nonselective oxidation for a small amount of CH_4 begins. When the temperature is over 350 °C, the concentration of H_2, CO and CO_2 suddenly increase, while the concentration of O_2 decreases to zero. In the range of 350–550 °C, the concentration of CO and CH_4 decreases, and the concentration of CO_2 remains nearly unchanged. The concentration of H_2 keeps an increase trend. The initial formation of CO_2 may be attributed to the total oxidation of dissociatively adsorbed CH_4 within 310–350 °C. At higher temperature above 450 °C, the dissociation of CH_4 is accelerated and thus the concentration of H_2 increases rapidly in the range of 450–700 °C. The high concentration of CO and H_2 at 350 °C in the low-temperature region might be due to the hot-spot over catalyst surface, which promoted the POM reaction. Within high temperature region (>550 °C), the concentrations of CO and H_2 increase with the temperature increase while the concentration of CO_2 decrease. It suggests that besides direct oxidation of methane, the high temperature (>550 °C) may also favors the endothermic reaction between CO_2 and CH_4.

Fig. 3b shows the reaction of methane with oxygen over pre-reduced Rh/SiO_2 catalyst. The result shows that the overall reaction trend is similar to that occurred over pre-oxidized catalyst. The difference is that the light up temperature drops to 330 °C. This result indicated that methane dissociation over rhodium sites might be the first step of the reaction, since metal rhodium have higher activity to split the carbon–hydrogen bond in methane, which might be the reason that reduced catalyst has lower light up temperature.

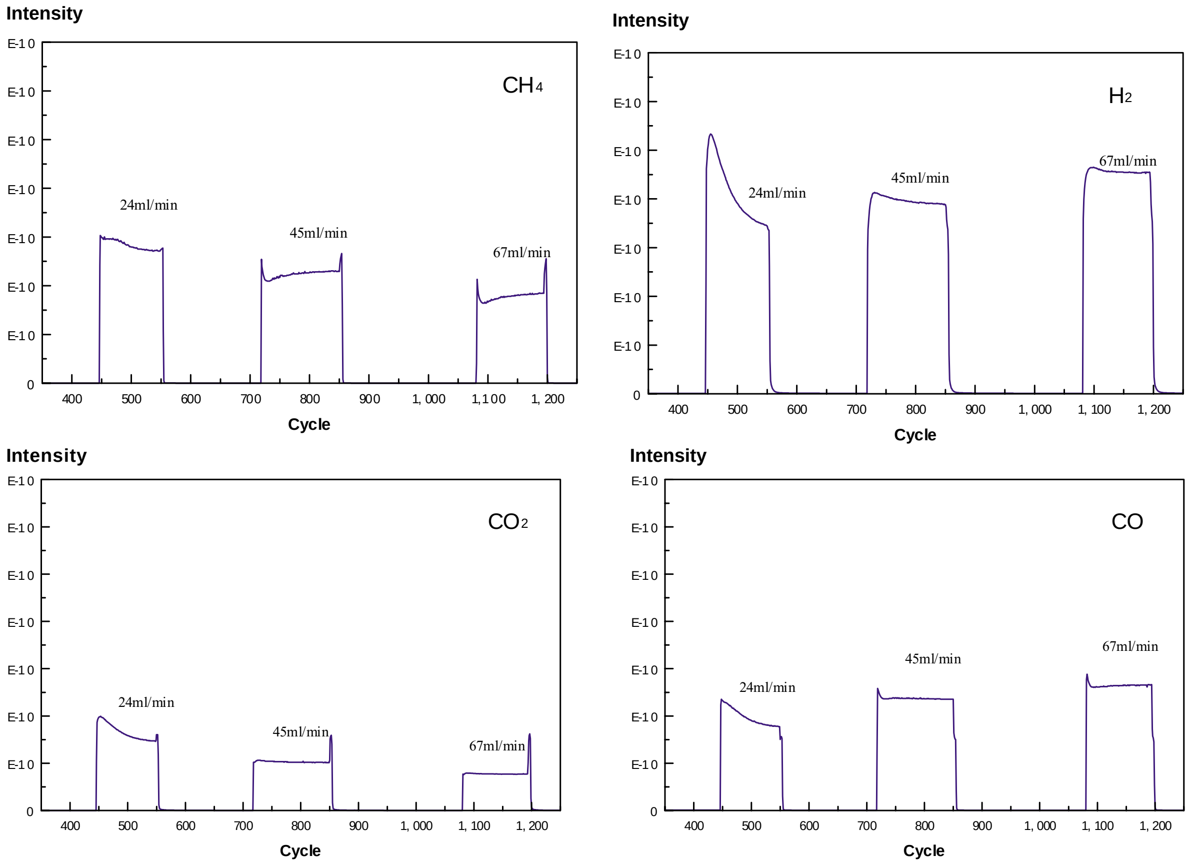

Fig. 4. Mass spectra over 1 wt.% Rh/SiO_2 catalyst after POM reactions were conducted in different space velocity at 500 °C.

3.4. *The influence of gas flow rate on POM*

Fig. 4 shows the influence of reactant gas (CH_4/O_2) flow rate on the conversion of methane and the selectivity of CO, CO_2, and H_2 at 500 °C. With the increase of gas flow rate, the conversion of methane and the selectivities of H_2 and CO increased, while the selectivity of CO_2 decreased. These results are similar to those that Hickman and Schmidt [12,21,22] reported over 10% Pt–Rh net catalyst. The results indicated that CO and H_2 might be the primary products. The decrease of CO_2 selectivity with the increase of the gas flow rate indicated that CO_2 might be deep oxidation product of CO.

3.5. *Interaction of methane with Rh/SiO_2 in pulse reactions*

Oxygen-free CH_4 pulse reaction was carried out over both pre-oxidized Rh/SiO_2 and pre-reduced Rh/SiO_2 at 700 °C. The mass spectra of the pulse reaction are shown in Fig. 5. The reaction results of methane with pre-oxidized catalyst are shown in Fig. 5a. High intensity peaks of CO and CO_2 were observed at the first methane pulse. However, almost no CO_2 was formed after the first pulse. It indicated that some of the oxygen species on the catalyst surface might be highly active at 700 °C. Even in the first pulse, almost all of the specific oxygen species were consumed. There might be trance amount of oxygen in the carrier gas, which leads to the generation of CO in the following pulses.

The reaction results of the pre-reduced catalyst with methane pulse at 700 °C are shown Fig. 5b. Similar response of CO and CO_2 were observed over catalyst. High CO_2 concentration was observed during the first pulse, and also, CO_2 appeared only at the first pulse over the reduced catalyst. However, the intensity of CO peak is much lower than that over the pre-oxidized Rh (O)/SiO_2 catalyst.

In pulse experiments, about 4.06×10^{-6} mol methane is introduced in each pulse (1 mL of 1/10 CH_4/Ar). According to the reaction of CH_4 with Rh_2O_3, unreduced Rh/SiO_2 catalyst will consume ca. 1.82×10^{-6} mol of CH_4. One pulse of methane would be more than enough to reduce all the rhodium oxide Rh_2O_3 species (ca. 4.9×10^{-6} mol) in 50 mg of the catalyst (∼1.0 wt.% Rh/SiO_2) to the metallic state. Therefore, part of the oxygen species on the catalysts responsible the conversion of CH_4 to carbon oxides from the second pulse onwards may come from the trace amount of O_2 or water vapor in He. The methane conversion would decrease because the active oxygen species was consumed quickly and couldn't be supplied efficiently for successive pulses. CO_2 couldn't be detected after the first pulse because concentration of the surface oxygen species was low. The oxygen from the carrier gas helium might only enough to generate CO after the first pulse. After the first pulse, the catalyst maintained a high CO selectivity, while the quantity of CO_2 is so small that it is below the detection limit of mass spectroscopy. This result indicated that CO is the primary oxidation product, while CO_2 is the secondary oxidation product. In addition, small amount of C_2H_4 and C_2H_6 can be detected during CH_4 pulsing reaction. They might come from partial dissociative adsorption of methane and consecutive coupling of CH_x ($x = 2, 3$) species. The quantity of C_2H_6 was always larger than that of C_2H_4 with the increase of pulse number. This might be due to that the dehydrogenation active center in the catalyst is gradually covered by the surface carbon species with more hydrogen, such as CH_3, which combined to form ethane. These result indicated that methane dissociated to CH_3-species and CH_2-species. CH_3-species couples to form ethane, while CH_2-species couples to form ethylene.

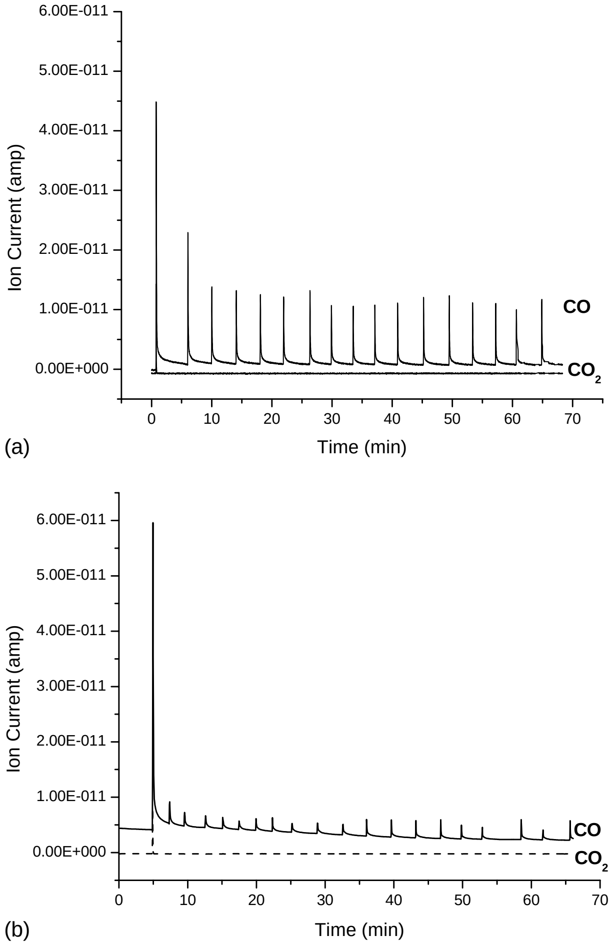

Fig. 5. CO and CO_2 produced by pulsing CH_4 at 700 °C over (a) the pre-reduced Rh/SiO_2 and (b) the pre-oxidized Rh (O)/SiO_2 catalyst.

3.6. *Interaction of CH_4/O_2/Ar with catalysts by transient reactions*

Transient experiments were performed at 500 and 700 °C at 1 atm with the step change from He to CH_4/O_2/Ar. The responses of the product distribution to the step changes are shown in Fig. 6a–d.

Fig. 6a shows the responses to a step change in the feed gas from helium to CH_4/O_2/Ar over pre-oxidized Rh (O)/SiO_2 at

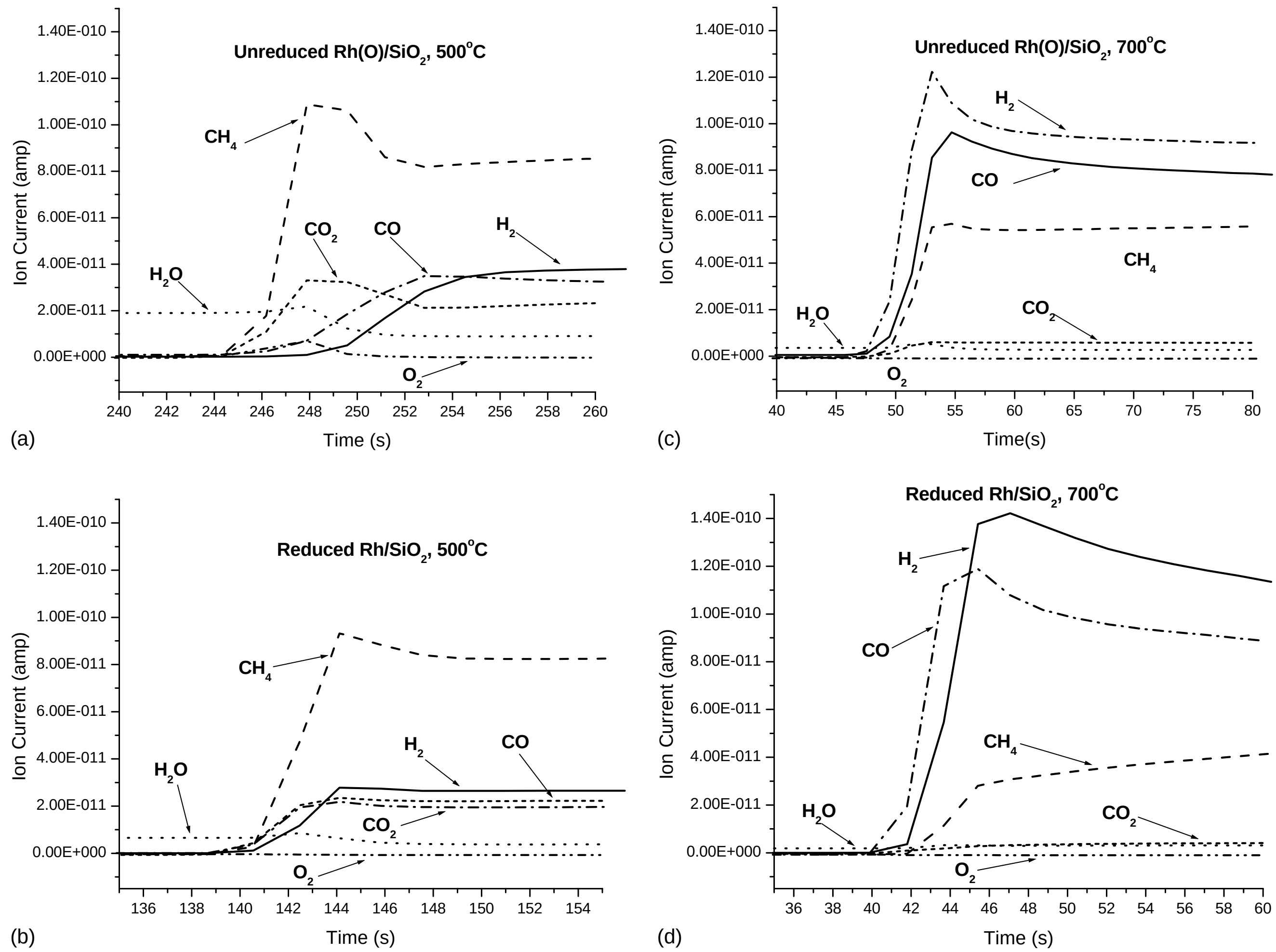

Fig. 6. Transient responses upon a step change in feed gas from He to $CH_4/O_2/Ar$ at 500 and 700 °C over (a) pre-oxidized Rh/SiO_2 at 500 °C, (b) pre-reduced Rh (O)/SiO_2 at 500 °C, (c) pre-oxidized Rh/SiO_2 at 700 °C, and (d) pre-reduced Rh (O)/SiO_2 at 700 °C.

500 °C. The concentrations of carbon dioxide and methane reached the maximum and then decline to a steady state, while carbon monoxide and hydrogen increase slowly then reach a steady-state level after the switch. Obviously, CH_4 and CO_2 appear before CO and H_2.

Fig. 6b shows the responses of the product effluents to a step change in the feed gas from helium to $CH_4/O_2/Ar$ obtained over the pre-reduced (500 °C, 30 min) Rh/SiO_2 catalyst. CO and H_2 appeared immediately and increased to a stable-state after the switch to $CH_4/O_2/Ar$. The amount of CO_2 increased to a stable level, but the quantity formed is lower than that of H_2 and CO.

Fig. 6c shows the responses to a step change in the feed gas from helium to $CH_4/O_2/Ar$ over oxidized Rh (O)/SiO_2 at 700 °C. CO and H_2 appeared immediately and quickly increased to a steady state after the change from helium to $CH_4/O_2/Ar$. The amount of CO_2 formed is less than that of H_2 and CO. At this case, hydrogen appeared before CO. The reason is not clear yet. More work is under planning.

Fig. 6d shows a plot of the products versus time as the same step change was made over the reduced Rh/SiO_2 catalyst at 700 °C. Carbon monoxide, hydrogen, and carbon dioxide appeared immediately after switching from He to $CH_4/O_2/Ar$. The hydrogen and carbon monoxide signals increased rapidly to reach their maximum, and then decreased slowly to a steady-state level. Only a small amount of CO_2 was detected after the step change reaction, which decreased quickly to the background level. However, at this case, CO appeared earlier than hydrogen. The reason is also not clear yet.

3.7. *Temperature program surface reaction*

Fig. 7 shows the temperature programmed hydrogenation (TPH) reaction of the surface carbon species formed on the Rh/SiO_2 surface, which was pre-reduced by CH_4 for at 700 °C. There are one weak peak and one strong peak at 200–250 and 450–900 °C, respectively. The TPH peak at low hydrogenating temperature (200–250 °C) should be corresponding to the carbon species with high H/C ratio (denoted as C_α, $\alpha = 1$–3). The TPH peak at high hydrogenation temperature (450–900 °C) should be corresponding to

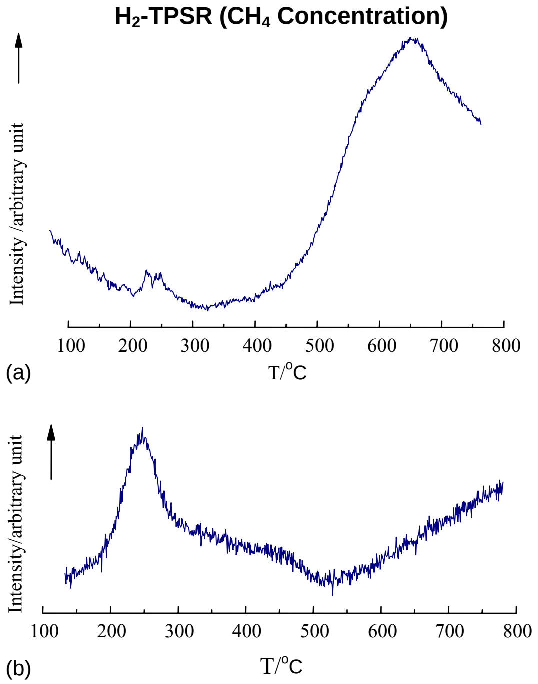

Fig. 7. TPSR profile on Rh/SiO_2 catalyst: (a) pre-treated by CH_4; (b) pre-treated by CH_4/O_2.

the carbon species with low H/C ratio, denoted as C_β ($0 \leq \beta < \alpha$). The concentration of C_β was higher than that of C_α, and also the result indicates that C_β species is more stable than C_α on the catalyst surface.

Fig. 7b shows the curve of temperature programmed hydrogenation reaction of the surface carbon species formed on Rh/SiO_2 pre-reacted with CH_4/O_2 at 700 °C. There was only one peak corresponding to C_α between 200 °C and 250 °C. The peak area of C_α between 200 °C and 250 °C in Fig. 7b is bigger than that in Fig. 7a.

It is well known that to break C–H bond of CH_4 on catalyst is the rate-determine step, while the oxidation of CH_x is a faster reaction. If C_β was the carbon species with less amount hydrogen atoms, they might be the further dissociation product of C_α species. If there was not oxygen co-feeding, there should be more C_α species converted to $C_{\beta.}$ This is consistent with experimental result. However, if oxygen was co-feed with methane, C_β species might be consumed quickly, the concentration of C_β species should be low. This is consistent with the reaction result.

4. Conclusion

The mechanism of methane partial oxidation to syngas on the Rh/SiO_2 catalyst can be summarized below. The oxygen species over the pre-oxidized catalyst could be oxygen in Rh_2O_3, RhO, and Rh_2O. They can be reduced at temperature below 140 °C by hydrogen. These rhodium oxides might decompose at high temperature (such as 700 °C) to generate active oxygen species, which is active enough to oxidize methane. Methane is first dissociated on Rh to generate the surface carbon species, such as CH_3–, CH_2– (CH_x, $x = 1$–3) with various H/C ratios, then the surface carbon species CH_x ($x = 1$–3) interacts with active oxygen species to generate CO, H_2, and $CO_{2.}$

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