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Mechanistic Studies of Methane Partial Oxidation to Syngas over SiO_2-Supported Rhodium Catalysts

C. T. Au[1] and H. Y. Wang

Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong

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The reaction behaviors of CH_4 and CH_4/O_2 (2/1) with reduced (Rh/SiO_2) and oxidized ($Rh(O)/SiO_2$) SiO_2-supported rhodium catalysts were investigated at temperatures ranging from 600 to 800°C over a pulse microreactor. The interaction of methane with Rh/SiO_2 led to CO, H_2 and surface carbon formation. The conversion of methane increased with the increase in rhodium loading. During the interaction of methane with $Rh(O)/SiO_2$ catalysts having rhodium loading $\geq$0.5%, besides CO, H_2, and surface carbon, CO_2 and H_2O were formed. Total oxidation of methane occurred over rhodium oxide together with the simultaneous reduction of Rh^{3+} to Rh^0. The partial oxidation of methane as well as the decomposition of methane took place over the resulting metallic rhodium. Within the first pulse of CH_4/O_2 (2/1), rhodium oxide in the oxidized catalysts was reduced to metallic rhodium. From the second pulse onward, both methane conversion and CO selectivity were similar to those observed over the reduced catalysts. The results indicate that metallic rhodium is the active site for methane partial oxidation and chemisorbed oxygen species have participated in the methane oxidation reaction. We suggest that OH groups and/or certain low coordinated oxygens of SiO_2 were also involved in the oxidation of methane, especially at low rhodium loadings. Deuterium isotope effects in the methane partial oxidation reaction were investigated at 700°C by performing $CH_4 + O_2$ and $CD_4 + O_2$ reactions alternately over the Rh/SiO_2 catalysts. Normal deuterium isotope effects of similar magnitude were observed on the overall reaction of methane oxidation as well as on the CO and CO_2 formation reactions with insignificant change in product selectivities. The results indicate that methane dissociation is a key step and that CO and CO_2 are formed via some common intermediates, viz. surface CH_x ($x = 0$–3) species. The activation energies for methane dissociation with or without the involvement of chemisorbed oxygen on a Rh(111) surface were calculated by means of the bond-order conservation Morse-potential approach.

1. INTRODUCTION

The conversion of methane to syngas is an important way to utilize methane. The steam reforming of methane over supported nickel catalysts operated above 800°C and 15 atm is the dominant commercialized method for syngas production (1, 2). The reaction is highly endothermic, and a mixture of CO and H_2 with a H_2/CO ratio of $\geq$3 is produced. Recently, the direct oxidation of methane to syngas has been investigated with renewed interest (3–19). The reaction is mildly exothermic and produces syngas with a H_2/CO ratio of about 2, a composition more suitable for methanol and Fischer–Tropsch syntheses. Thus, the direct oxidation of methane is more energy efficient and can produce a H_2/CO ratio more desirable than that obtained in steam reforming. Conversions close to equilibrium values can be achieved for the direct oxidation reaction over supported noble metals such as Rh, Ru, Pd, Pt, and supported Ni catalysts. Rhodium is supposed to be the only metal which gives high and stable syngas yield (13).

Concerning the reaction pathway for methane partial oxidation to syngas, several reaction schemes have been suggested. Many researchers (3, 4, 10, 12, 14) favored the idea of Prettre *et al.* (20), who proposed that two stages are involved: (i) complete oxidation of methane to CO_2 and H_2O, and (ii) reforming of the remaining methane by H_2O and/or CO_2 formed in the first stage. Schmidt and co-workers (7, 8, 11, 13) suggested that syngas is formed directly in methane oxidation without the involvement of CO_2. They proposed a mechanism of catalytic methane pyrolysis followed by surface carbon oxidation and hydrogen desorption. Choudhary and co-workers (5, 6) also advocated the direct oxidation of methane to syngas. Buyevskaya *et al.* (15), however, suggested that CO is formed via a fast reaction of surface carbon species with CO_2; both are primary products of methane interaction, respectively, with reduced and oxidized surface rhodium sites.

Concerning the active sites for methane partial oxidation to syngas, Lunsford and co-workers (4) proposed that the unreduced NiO/Al_2O_3 and the reduced Ni/Al_2O_3 were, respectively, the active sites for the initial complete oxidation of methane and for the consecutive reforming reactions of methane. Buyevskaya *et al.* (15) suggested that reduced and oxidized surface rhodium were active sites for methane decomposition to surface carbon and methane complete oxidation to CO_2, respectively. Mallens *et al.* (17) have studied the reactivity of three different

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[1] To whom correspondence should be addressed. Fax: H.K. 23397348.

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types of oxygen, viz. platinum oxide, dissolved oxygen, and chemisorbed oxygen, and concluded that syngas is produced from methane via oxygen present as platinum oxide. In our previous studies (19), we proposed that metallic nickel in reduced Ni/SiO_2 catalyst was active for methane decomposition and syngas formation.

As reported by Dissanayake *et al.* (21) and by Chang and Heinemann (10), a large thermal gradient as much as 300–600°C (or hot spots) could be created in the catalyst bed during the oxidation of methane at high space velocities. Thus, it is hard to identify reliably the reaction mechanism from data obtained in conditions where hot spots might be a problem. Boucouvalas *et al.* (14) heavily diluted both the feed gas and the solid catalyst to ensure the absence of hot spots in their mechanistic studies of methane partial oxidation. The pulse technique has also been used by many researchers to lessen the problem (15–19). Since the amount of reactant(s) pulsed in each time over the catalyst is small, the problem of hot spots can be avoided.

The aim of the present study was to investigate the reaction mechanism and the nature of the active site for the partial oxidation of methane over rhodium catalysts, using the pulse and BOC–MP methods. The reaction behaviors of CH_4 and CH_4/O_2 with reduced and oxidized rhodium catalysts were compared in the 600 to 800°C range. Furthermore, deuterium isotope effects were investigated by performing the $CH_4 + O_2$ and $CD_4 + O_2$ reactions alternately over the reduced catalysts to probe the mechanistic aspects of methane partial oxidation to syngas.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The SiO_2-supported rhodium catalysts were prepared by impregnating SiO_2 granules (Aldrich, 0.2–0.3 mm, 406 m^2/g) with $RhCl_3 \cdot 3H_2O$ (Beijing Chemical Institute) methanol solution, followed by drying at 110°C for 12 h and calcining at 500°C for 2 h for decomposition. The catalysts so prepared were the oxidized ones and are signified as Rh(O)/SiO_2. The catalysts further treated in H_2 at 500°C for 1 h were the reduced ones and are expressed as Rh/SiO_2. The dispersion of rhodium for Rh/SiO_2 catalysts was determined by means of H_2–O_2 titration at room temperature and the results are listed in Table 1.

TABLE 1

Characteristic of Catalysts

Rh loading (wt%)	Dispersion[a] (%)	Particle diameter[b] (nm)	Specific metal area (m^2-Rh/g-cat)
0.05	100[c]	<1.1	0.23
0.2	96.2	1.11	0.89
0.5	85.7	1.25	1.98
1.0	67.5	1.59	3.12
2.0	49.8	2.15	4.60
4.0	32.7	3.27	6.04
8.0	26.0	4.12	9.61

[a] Assuming an adsorption stiochiometry of H(O) : Rh = 1 : 1.
[b] Assuming a hemispherical model for metal particles.
[c] Estimated.

2.2. Pulse Reaction

The apparatus for pulse reaction has been described previously (16), only the reactor used this time was made of quartz tubing with 4 mm i.d. During the pulse experiments, there was a constant flow of helium (flow rate, 17 ml/min) through the reactor, and the reactant gas mixture was flushed in by the carrier gas. The time interval between pulses during the pulse experiments of CH_4/O_2 (2/1) was 12 min. For the pulse experiments of CH_4 over the reduced catalysts, it was 5 min. For the pulse experiments of CH_4 over the oxidized catalysts, the time interval was 12 min between the first and the second pulse and was 5 min between pulses thereafter. For each study, 50 mg of catalyst was used, and the pulse volumes of methane and methane/oxygen (2/1) were 1.11 and 1.03 ml, respectively. The reactants and products were analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with TCD (MS5A and Porapak Q as columns). The blank runs with CH_4/O_2 (2/1) mixture showed almost no activity at or below 700°C, and ca. 6.5% of methane conversion at 800°C due to gas-phase reaction. For each experiment, the conversion of methane (X) was defined as $X_{CH_4} = (n_{in,CH_4} - n_{out,CH_4})/n_{in,CH_4}$, where n is the total amount of molecules (mol). Selectivities (mol%) were calculated on the basis of carbon contents in the products.

As pointed out by Schmidt and co-workers (7), mass transfer limitations can be eliminated at low pressures. Since the reactant(s) in the pulse reaction had been diluted by the carrier gas before passing the reactor, one might expect the effects of mass transfer were not significant.

2.3. Investigation of Deuterium Isotope Effects

The experiment was carried out in such a manner that CH_4/O_2 (2/1) was first pulsed over the prereduced catalyst to perform the $CH_4 + O_2$ reaction. After the eighth CH_4/O_2 pulse, $CD_4 + O_2$ reaction was carried out by pulsing in CD_4/O_2 instead. After the eighth pulse of CD_4/O_2, the $CH_4 + O_2$ reaction was carried out again. By performing the $CH_4 + O_2$ and $CD_4 + O_2$ reactions alternately in this way, deuterium isotope effects were investigated. Average values of methane conversion and yields of CO and CO_2 in the $CH_4 + O_2$ and $CD_4 + O_2$ reactions were calculated with the exclusion of the first two points in each set of eight reaction points. The relative ratios of methane conversion, CO and CO_2 yields in the $CH_4 + O_2$ reaction to the corresponding ones in the $CD_4 + O_2$ reaction are used to express the magnitude of isotope effects.

2.4. *BOC–MP Approach*

The bond-order conservation Morse-potential approach was developed by Shustorovich (22). It has been applied successfully in the calculations of adsorption heats of reactants, intermediates and products as well as activation energies for elementary processes over transition metals (23–25). In the present case, the BOC–MP method was used to evaluate the activation energies and reaction enthalpies for the elementary steps of methane dissociation with or without the involvement of chemisorbed oxygen on Rh(111) surface.

3. RESULTS

3.1. *Interactions of CH_4 with Rh/SiO_2 and $Rh(O)/SiO_2$*

The interactions of methane pulses with the reduced and the oxidized catalysts were investigated at 700°C. Over the reduced catalysts, H_2 and CO were detected. When O_2 was pulsed in instead after the 18th pulse of methane, CO and CO_2 were detected over the Rh/SiO_2 catalysts with Rh loadings higher than 0.05%, signifying the generation of surface carbon species during the previous interaction of methane. The amount of surface carbon formed at each reaction point was evaluated according to the carbon balance. Over the oxidized catalysts, except for the catalyst with 0.05% Rh loading, CO_2 and H_2O were formed besides CO, H_2 and surface carbon during the first reaction point of methane. From the second reaction point onward, the products formed over the oxidized catalysts were similar to those observed over the reduced catalysts.

In Fig. 1, the reaction behaviors of CH_4 with the reduced and the oxidized catalysts during the first reaction point were compared. Over the reduced catalysts, with the increase of rhodium loading from 0.05 to 8.0%, methane conversion increased from ca. 5 to ca. 40% and the selectivity of surface carbon increased from 0 to ca. 84%, whereas CO selectivity decreased from 100 to ca. 16%. Over the oxidized catalysts, with the increase in Rh loading from 0.05 to 8.0%, methane conversion increased from ca. 6.5 to ca. 70% and CO_2 selectivity increased from 0 to ca. 40%, while CO selectivity decreased from ca. 86 to ca. 26% and the selectivity of surface carbon exhibited a maximum value at 2.0% rhodium loading. At the first reaction point, the molar ratios of rhodium oxide to CH_4 pulse size (Rh_2O_3/CH_4) over the four oxidized catalysts with 0.05, 0.5, 2.0, and 8.0% Rh loadings were estimated to be 0.002, 0.02, 0.10, and 0.36, respectively. The yields of CO_2 over these catalysts were 0, 1.3, 6.1, and 27.9%. So, there was a parallel relation between the molar ratio of Rh_2O_3/CH_4 and the activity for CO_2 formation. From Fig. 1, it can also be seen that methane conversion was higher over $Rh(O)/SiO_2$ than that over Rh/SiO_2 for the same rhodium loadings, indicating that rhodium oxide has higher ability for methane conversion than metallic rhodium.

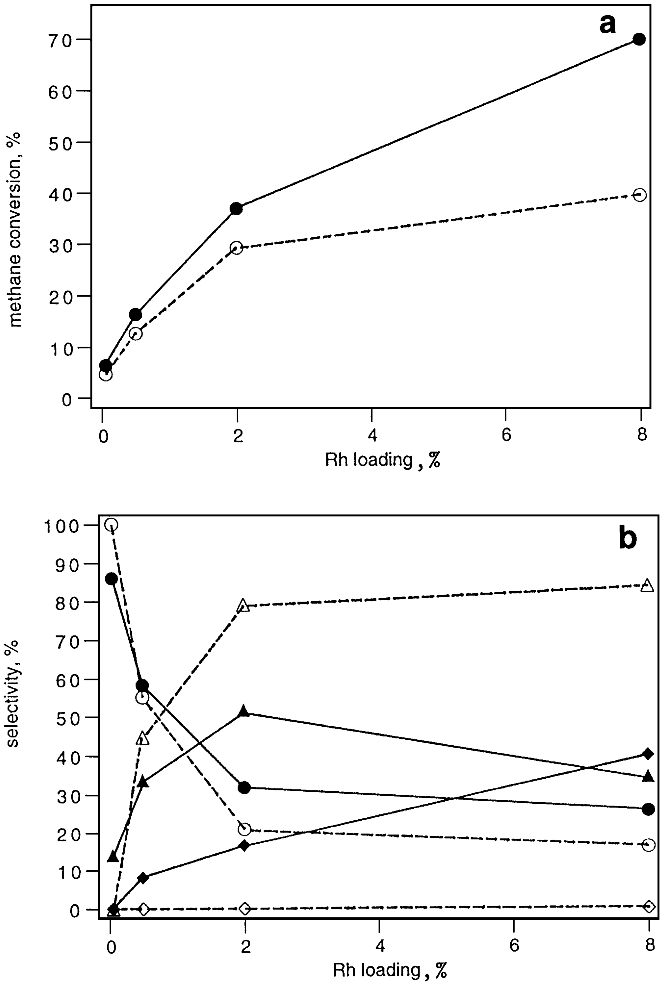

FIG. 1. Comparison of (a) methane conversion and (b) CO (○), surface carbon (△), and CO_2 (◇) selectivities during the first reaction point of CH_4 over Rh/SiO_2 (open symbols) and $Rh(O)/SiO_2$ catalysts (solid symbols) at 700°C. The turnover frequencies for methane conversion over the reduced Rh/SiO_2 catalysts with 0.05, 0.5, 2.0, and 8.0% rhodium loadings are 2.46, 0.77, 0.77, and 0.54 s^{-1}, respectively.

Figure 2 shows the variation of methane conversion and the yield of surface carbon over the Rh/SiO_2 catalysts as related to the number of methane pulses. During the first six reaction points, both methane conversion and the yield of surface carbon increased greatly with the increase in rhodium loading from 0.05 to 8.0%. For the Rh/SiO_2 catalysts having rhodium loading $\geq 0.5\%$, one can see that during the first six reaction points, with the increase in methane pulse number, the higher the rhodium loading was, the faster would be the decrease in methane conversion and the yield of surface carbon. The results indicate that the catalysts with higher rhodium loading have higher ability for methane dissociation and the occupancy of the active

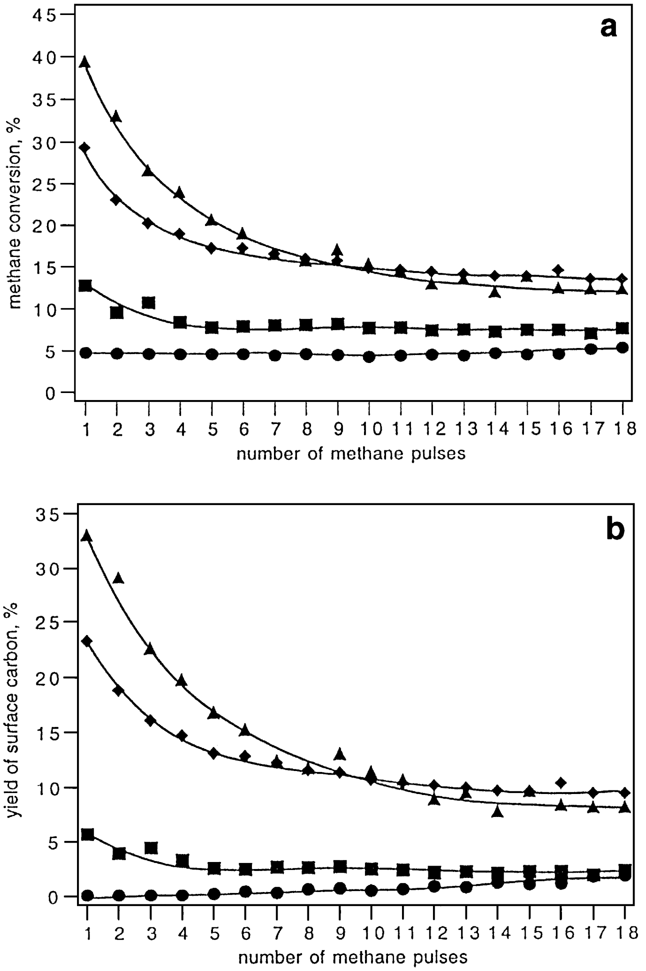

FIG. 2. The relationship of (a) methane conversion and (b) surface carbon yield with the number of methane pulses over 0.05% Rh/SiO_2 (●), 0.5% Rh/SiO_2 (■), 2.0% Rh/SiO_2 (◆), and 8.0% Rh/SiO_2 (▲) at 700°C. The turnover frequencies for methane conversion during the first reaction point of methane over the reduced catalysts with 0.05, 0.5, 2.0, and 8.0% rhodium loadings are 2.46, 0.77, 0.77, and 0.54 s^{-1}, respectively. The corresponding turnover frequencies for surface carbon formation are 0, 0.35, 0.61, and 0.45 s^{-1}, respectively.

sites by carbon species could be the reason for the decline in methane conversion. Over the $Rh(O)/SiO_2$ catalysts, from the second pulse of methane onward, the patterns of methane conversion and the yield of surface carbon were similar to that over the reduced catalysts, indicating that rhodium oxide was largely reduced to metallic rhodium during the first reaction point.

3.2. *Interactions of CH_4/O_2 with Rh/SiO_2 and $Rh(O)/SiO_2$*

The simultaneous interactions of methane and oxygen with the reduced and the oxidized catalysts were investigated by pulsing in CH_4/O_2 mixture with a stoichiometric feed ratio of 2/1. The products formed were CO, H_2, CO_2, and H_2O. According to the result of carbon balance, it can be assumed that no carbon was deposited on the catalyst surface after each reaction point.

In Fig. 3, the reactivities of CH_4/O_2 over 2.0% Rh/SiO_2 and over 2.0% $Rh(O)/SiO_2$ were compared at temperatures ranging from 600 to 800°C. At the first reaction point, methane conversion over the latter was higher than that over the former and CO selectivity over the latter was ca. 25% lower than that over the former regardless of reaction temperature. From the second CH_4/O_2 pulse onward, CO was the primary carbon-containing product, and both methane conversion and CO selectivity over the oxidized catalyst were comparable with that over the reduced one. Over catalysts with 0.5 and 8.0% rhodium loadings, similar results were observed. Over the catalyst with 0.05% rhodium loading, as the amount of Rh_2O_3 in the oxidized catalyst was very low, the differences between methane conversions and between CO selectivities over the reduced and

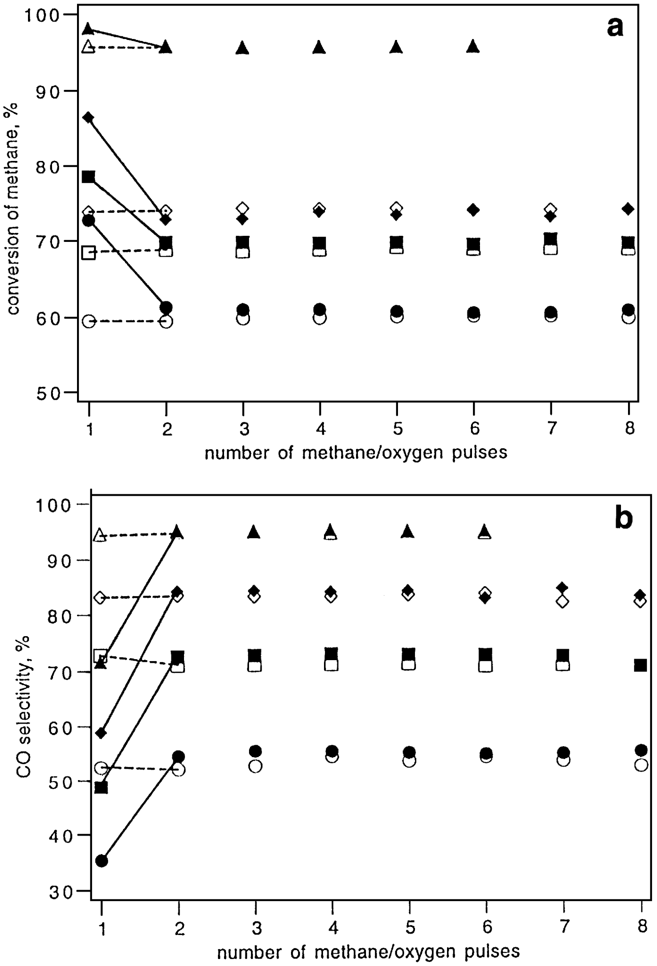

FIG. 3. Comparison of (a) methane conversion and (b) CO selectivity during $CH_4 + O_2$ reaction over 2.0% Rh/SiO_2 (open symbols) and 2.0% $Rh(O)SiO_2$ (open symbols) at 600 (○), 650 (□), 700 (◇), and 800 (△)°C. The turnover frequencies for methane conversion during the first reaction point of CH_4/O_2 at 600, 650, 700, and 800°C are 1.04, 1.20, 1.29, and 1.68 s^{-1}, respectively.

oxidized catalysts were not significant. In Fig. 4, the reaction behaviors of CH_4/O_2 over the reduced and the oxidized catalysts during the first reaction point were compared. For the reduced catalysts, no significant changes in methane conversion and in CO selectivity were observed when rhodium loading was increased from 0.5 to 8.0%, whereas over the oxidized catalysts, methane conversion increased greatly and CO selectivity decreased significantly.

3.3. *Deuterium Isotope Effects in Methane Partial Oxidation Reaction*

Deuterium isotope effects were investigated over the Rh/SiO_2 catalysts at 700°C by performing the $CH_4 + O_2$ and $CD_4 + O_2$ reactions alternately. Figure 5 shows the variations of methane conversion, yields of CO and CO_2, and CO selectivity over a 0.5% Rh/SiO_2 catalyst at 700°C as a function of the number of methane/oxygen pulses. As shown in Fig. 5a, when $CH_4 + O_2$ reaction was alternated to $CD_4 + O_2$, methane conversion decreased noticeably (by ca. 6%); conversely, when $CD_4 + O_2$ was changed to $CH_4 + O_2$, methane conversion increased distinctly, indicating the overall reaction of methane oxidation showed a normal deuterium isotope effect. From Figs. 5b and 5c, one can see that the yields of both CO and CO_2 showed the same trend as methane conversion, indicating that both CO and CO_2 formation reactions showed normal deuterium isotope effects in methane partial oxidation reaction. Methane conversion, CO and CO_2 yields in the $CH_4 + O_2$ reaction were all about 1.08 times that in the $CD_4 + O_2$ reaction. As shown in Fig. 5d, with the exclusion of the first reaction point of CH_4/O_2 pulses where stable state has not yet been reached, CO selectivity (CO_2 as well, though not shown) stayed at almost the same level, meaning no significant change in product selectivities occurred during the alternations of $CH_4 + O_2$ and $CD_4 + O_2$ reactions. Over other reduced rhodium catalysts with different Rh loadings, similar results were observed.

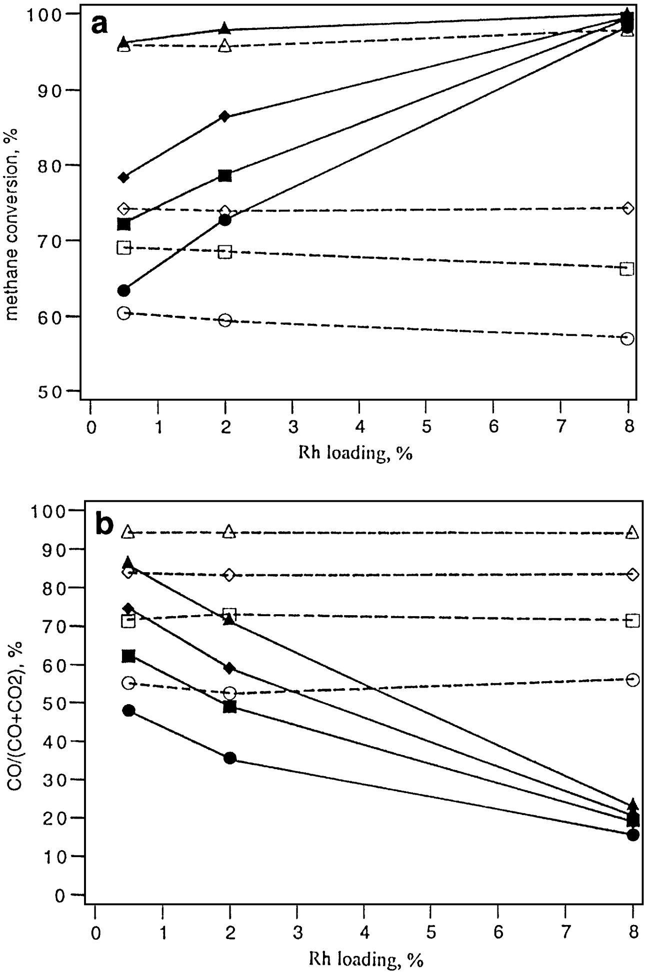

FIG. 4. Comparison of (a) methane conversion and (b) CO selectivity during the first reaction point of CH_4/O_2 over Rh/SiO_2 catalysts (open symbols) and $Rh(O)/SiO_2$ catalysts (solid symbols) at 600 (○), 650 (□), 700 (◇), and 800 (△)°C. The turnover frequencies for methane conversion at 800°C over the reduced Rh/SiO_2 catalysts with 0.5, 2.0, and 8.0% rhodium loadings are 3.89, 1.68, and 0.87 s^{-1}, respectively.

TABLE 2

Activation Energies (ΔE^*) and Reaction Enthalpies (ΔH) for Methane Direct Dissociation on Rh(111) Surface (kJ/mol)

Reaction	ΔE^*	ΔH
$CH_{4,s} \rightarrow CH_{3,s} + H_s$	61	10
$CH_{3,s} \rightarrow CH_{2,s} + H_s$	103	59
$CH_{2,s} \rightarrow CH_s + H_s$	100	32
$CH_s \rightarrow C_s + H_s$	21	−146

3.4. *Activation Energies for Methane Dissociation on Rh(111) Surface*

The activation energies for methane dissociation on Rh(111) with or without the involvement of oxygen were calculated by means of the BOC–MP approach and the results are presented in Tables 2 and 3. Three types of

TABLE 3

Activation Energies (ΔE^*) and Reaction Enthalpies (ΔH) for Methane Dissociation with the Involvement of Chemisorbed Oxygen on Rh(111) Surface (kJ/mol)

	ΔE^*			ΔH		
Reaction	On-top	Bridge	Hollow	On-top	Bridge	Hollow
$CH_{4,s} + O_s \rightarrow CH_{3,s} + OH_s$	0	56	77	−120	8	51
$CH_{3,s} + O_s \rightarrow CH_{2,s} + OH_s$	31	95	116	−71	57	100
$CH_{2,s} + O_s \rightarrow CH_s + OH_s$	25	89	111	−98	30	73
$CH_s + O_s \rightarrow C_s + OH_s$	0	33	61	−276	−148	−105

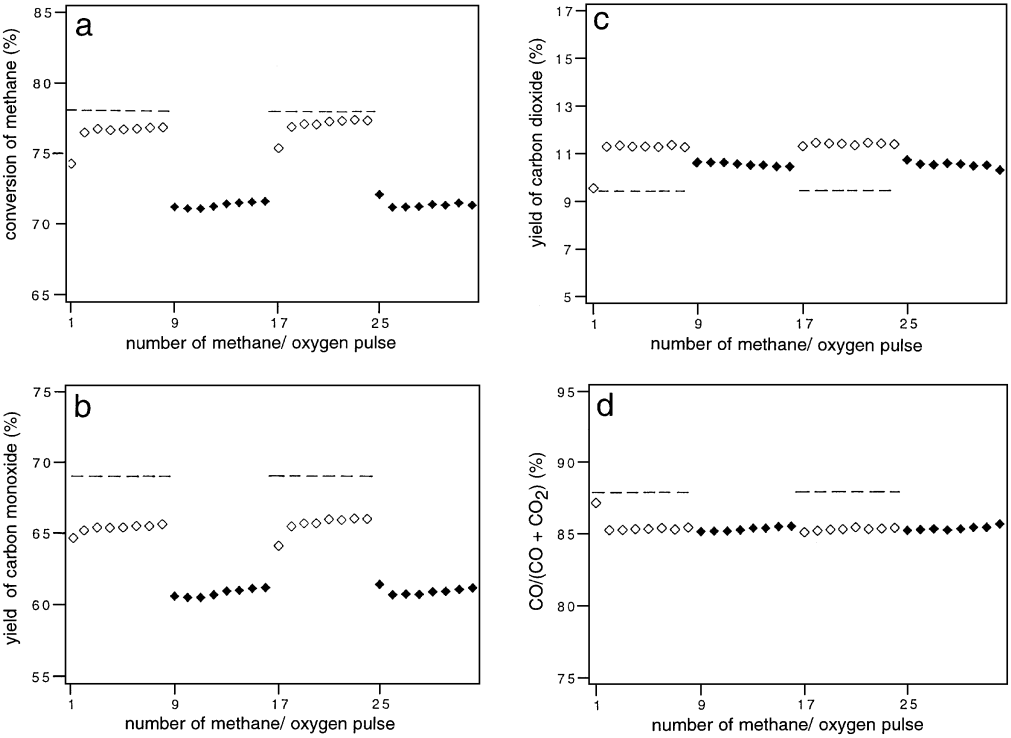

FIG. 5. The relationship of (a) methane conversion, (b) CO yield, (c) CO_2 yield, and (d) CO selectivity with the number of methane/oxygen (open symbols for CH_4/O_2, solid symbols for CD_4/O_2) pulses over 0.5% Rh/SiO_2 at 700°C. Also added in dash lines are the equilibrium values (4) for CH_4 conversions, selectivities and yields for the $CH_4 + O_2$ reaction. For the $CH_4 + O_2$ reaction, the turnover frequencies for methane conversion, CO and CO_2 yields are 3.11, 2.65, and 0.57 s^{-1}, respectively. For the $CD_4 + O_2$ reaction, they are, respectively, 2.89, 2.47, and 0.53 s^{-1}.

adsorbed oxygen species located at on-top, bridge and hollow sites were considered. The results indicate that the direct dissociation of methane on Rh(111) is strongly activated. As shown in Tables 2 and 3, in comparison with the direct dissociation of methane, methane dissociation reactions involving O_s located at on-top sites have lower activation energies and reaction enthalpies, while those involving O_s at hollow sites have higher activation energies and are more endothermic.

4. DISCUSSION

4.1. *Active Site for Methane Partial Oxidation to Syngas*

During the first reaction point of methane with the reduced catalysts, at 0.05 and 0.5% rhodium loadings, CO formation dominated, while at 2.0 and 8.0%, methane decomposition and surface carbon accumulation prevailed (Fig. 1). The results indicate that there were two kinds of catalytic reactions for methane, viz. partial oxidation to CO and decomposition to surface carbon species over the reduced catalysts. Since there was no oxygen in the feed, the formation of CO indicates that OH surface groups and/or certain low coordinated oxygens of the SiO_2 support had participated in methane conversion to CO. Similar results have been reported previously by Buyevskaya *et al.* (15). They concluded that OH surface groups of the support can be involved in the conversion of CH_x to CO via reforming reaction over 1 wt% Rh/Al_2O_3 catalyst. Since pure SiO_2 showed no activity at 700°C toward methane conversion, the activation of methane by reduced rhodium sites is required for the reaction of methane with surface OH groups and/or low coordinated oxygens of SiO_2 support to form CO.

Different from the situations over the reduced catalysts, total oxidation products, viz. CO_2 and H_2O were formed during the first reaction point over the oxidized catalysts with rhodium loadings $\geq$0.5% and CO_2 selectivity increased with the increase in rhodium loading (Fig. 1). Since there was a parallel relationship between the molar ratio of Rh_2O_3/CH_4 and the activity for CO_2 formation, it can be inferred that rhodium oxide is responsible for the formation of CO_2 and H_2O. As pointed out by Haber (26), total oxidation of hydrocarbons is often observed over transition metal oxides even in the absence of gaseous oxygen. Hence, it is reasonable to deduce that during the first reaction point, stoichiometric redox reaction ($4Rh_2O_3 + 3CH_4 = 8Rh + 3CO_2 + 6H_2O$) between methane and rhodium oxide in the oxidized catalysts occurred, leading to the total oxidation of methane and the reduction of rhodium oxide. It has been reported elsewhere (19) that reduced Cu/SiO_2 was inactive for methane decomposition and during the interaction of methane with the oxidized CuO/SiO_2 catalyst, only the total oxidation products, viz. CO_2 and H_2O were formed. In the present work, reduced Rh/SiO_2 was observed to be active for methane decomposition and besides CO_2 and H_2O, CO was also detected during the interaction of methane with the $Rh(O)/SiO_2$ catalysts. The contrast between copper and rhodium catalysts indicates that methane dissociation is indeed a key step for CO formation. We suggest that CO formation proceeds via CH_x ($x = 0$–3) species produced by methane dissociation over the Rh^0 sites. Thus, during the first reaction point of methane with the oxidized catalysts having rhodium loading $\geq 0.5\%$, there were three kinds of reactions for methane, viz. complete oxidation to CO_2 over rhodium oxide (simultaneous reduction of Rh^{3+} to Rh^0), partial oxidation to CO and decomposition to surface carbon species over the resulting metallic rhodium.

For the reactions of CH_4/O_2 (2/1) over the reduced and the oxidized catalysts, similar reactivities were observed from the second reaction point onward (Section 3.2). Similar to those observed during the first reaction point of methane with $Rh(O)/SiO_2$, CO selectivity decreased and CO_2 selectivity increased with the increase in Rh loading during the first reaction point of CH_4/O_2 over the $Rh(O)/SiO_2$ catalysts (Fig. 4). Thus, it can be deduced that the oxidized rhodium was almost reduced to metallic rhodium by methane during the first reaction point of CH_4/O_2 and from the second reaction point onward, reaction actually occurred on the reduced rhodium sites. The results clearly indicate that metallic rhodium is the active site for methane partial oxidation to syngas. This is somewhat different from the viewpoint of Buyevskaya *et al.* (15) who suggested that the active sites for methane partial oxidation over 1% Rh/Al_2O_3 were surface oxygen. In their mechanistic studies using transient pulse technique, they concluded that the overall reaction occurred via a redox mechanism and the role of gas-phase oxygen is to replenish the active sites on the surface after depletion of oxygen due to reaction with methane.

Mallens *et al.* (17) have reported that no significant amount of CO formation was observed during pulse experiment of CH_4/O_2 with stoichiometric feed ratio over reduced platinum catalyst and deduced that oxygen was incorporated into the catalyst. They considered the observation as an indication that platinum oxide must be present for the formation of syngas. In the present work, however, we find that metallic rhodium is needed for syngas formation. According to Fig. 1, rhodium oxide has higher ability for methane conversion than metallic rhodium. So if indeed certain amount of metallic rhodium was oxidized to rhodium oxide during a reaction point of CH_4/O_2, CO selectivity would have to decrease in the next reaction point due to methane total oxidation over rhodium oxide. But this was not the case. As shown in Fig. 3, over a 2.0% Rh/SiO_2 catalyst, CO was formed as the primary carbon containing product and both methane conversion and CO selectivity were fairly constant as a function of the number of CH_4/O_2 pulses. Over other Rh/SiO_2 catalysts, similar results were observed. Thus, we conclude that rhodium can keep its original reduced state during methane partial oxidation reaction and metallic rhodium is actually the active site for syngas formation. In view of this, it can also be assumed that chemisorbed oxygen species are involved in the oxidation of methane. As observed in Section 3.1, during the interaction of methane with the reduced Rh/SiO_2 catalysts, CO can be formed via the reaction of methane with OH groups and/or some low coordinated oxygens of SiO_2. Hence the role of SiO_2 oxygen sites in the $CH_4 + O_2$ reaction should also be taken into account, especially when rhodium loading is low.

4.2. *Reaction Mechanism of Methane Partial Oxidation to Syngas*

As discussed in the Introduction, a unified mechanism for methane partial oxidation has not been reached so far. The main controversy on the mechanism is whether syngas is directly formed or is formed via the involvement of CO_2. CO_2 was believed to be formed in the total oxidation reaction of methane (3, 4, 10, 12, 14, 15). It was also regarded as the secondary product of CO further oxidation in the methane pyrolysis mechanism proposed by Schmidt and co-workers (7, 8, 11, 13). Hu and Ruckenstein (27) have observed delay in CO_2 generation in comparison to CO generation in the transient response curves of the products in a CH_4/O_2 pulse at 500°C over the reduced 20% Ni/La_2O_3 catalyst. They concluded that CO is the primary product and CO_2 is only subsequently generated from CO. In the present work, the pathways for the formation of CO and CO_2 are discussed based on the results of deuterium isotope experiments.

The overall reaction of methane oxidation as well as the CO and CO_2 formation reactions were observed to show normal deuterium isotope effects of similar magnitude when CD_4 was used instead of CH_4 to perform the methane partial oxidation reaction (Figs. 5a–5c). Generally speaking (28), when a bond to hydrogen is broken in the rate-determining step of a reaction, a normal deuterium isotope effect will be expected. Thus, it can be concluded that methane dissociation is a key step and that CO and CO_2 are formed via some common intermediates, whose formations are subject to deuterium isotope effect. Obviously, these common intermediates are surface CH_x ($x = 0$–3) species originated from methane decomposition. These conclusions are compatible with the methane pyrolysis mechanism. In addition, the pattern of the change in product selectivities observed during the alternations of $CH_4 + O_2$ and

$CD_4 + O_2$ reactions can be reasonably explained based on the following methane pyrolysis mechanism:

$$\begin{tikzcd}
CH_{4,g} \arrow[r] & CH_{x,s} \arrow[r, "O_s"] & CO_s \arrow[r] \arrow[d, "O_s"] & CO_g \\
 & & CO_{2,s} \arrow[r] & CO_{2,g}
\end{tikzcd}$$

According to the above mechanism, CO and CO_2 selectivities are mainly governed by the following two competitive reactions, viz. the desorption of CO_s to CO_g and the further oxidation of CO_s to $CO_{2,s}$. When CD_4 is used instead of CH_4, the dissociation rate of methane and the formation rates of surface CH_x species decrease simultaneously due to deuterium isotope effect, leading to the decrease in the formation rates of CO_s and $CO_{2,s}$. On the other hand, the relative rate of CO_s desorption to CO_s further oxidation is free from deuterium isotope effect and remains almost unchanged, resulting in similar product selectivities (Fig. 5d). Therefore, the methane pyrolysis mechanism is upheld in the present work. The investigations of deuterium isotope effects reported so far should be seen as a qualitatively approach as the partial oxidation reactions were conducted close to thermodynamic equilibrium conditions (X_{CH_4} ∼90%, 700°C). Under such conditions, the extent of the reverse reaction, viz. $CO + H_2$ (or D_2) to CH_4 (or CD_4), should be reckoned as significant. Thus, the influence of deuterium isotope effects on the reverse reaction should be taken into account. Qualitatively, while the rate of the forward reaction decreases due to the normal deuterium isotope effect (28), the rate of the reverse reaction increases due to the inverse deuterium isotope effect (29). Hence when the reaction is getting close to equilibrium, these relative rates must be viewed with caution. The counteraction of these two opposing effects might be the reason for the fairly small magnitude of the net deuterium isotope effects observed in the present study. It is clear that experiments performed at lower methane conversions under the kinetic-controlling regime would be more desirable in this aspect.

In the process of methane partial oxidation to syngas, C−H bonds in methane should be broken before CO formation. Schmidt and co-workers (7, 8, 11, 13) believed that methane pyrolysis was the primary pathway for methane dissociation. As reported in Sections 3.1 and 3.2, the activity of methane dissociation increased with the increase in rhodium loading (Fig. 2); while the activity for methane partial oxidation to syngas was almost unaffected by the loading of rhodium (Fig. 4). Schmidt and co-workers (8) have also reported that for rhodium catalysts, the selectivities and activities were almost identical for Rh loadings between 1 and 15%. As disclosed in the investigation of deuterium isotope effects, methane dissociation is a key step for syngas formation in the process of methane partial oxidation. Hence, it can be inferred that direct dissociation is not the only pathway for methane dissociation. Solymosi and co-workers (30) have observed that the addition of CO_2 to CH_4 greatly promoted the dissociation of CH_4 over supported Rh catalysts. They assumed that the dissociation of CH_4 was facilitated by adsorbed O generated in the decomposition of CO_2. In other words, besides the direct dissociation of methane, oxygen-assisted dissociation could be another pathway for methane dissociation.

The results of Tables 2 and 3 indicate that methane dissociation reactions involving O_s located at on-top sites have lower activation energies and reaction enthalpies, while those involving O_s at hollow sites have higher activation energies and are more endothermic in comparison with the direct dissociation of methane. The results suggest that the oxygen species at on-top sites can promote methane dehydrogenation while those at bridge and hollow sites are not beneficial for methane dissociation on Rh surface.

As shown in Table 1, rhodium dispersion decreased with the increase in rhodium loading. It can be reckoned that the relative ratio of the amount of adsorbed oxygen at the on-top sites to the amount of that at the hollow sites decreases with the increase in rhodium loading. We suggest that over the Rh/SiO_2 catalysts with low rhodium loadings (e.g., 0.05 and 0.5%), oxygen-assisted dissociation of methane dominates; while over the catalysts with high rhodium loadings (e.g., 2.0 and 8.0%), methane dissociation can be direct as well as oxygen-assisted.

5. SUMMARY

Based on the reaction behaviors of CH_4 and CH_4/O_2 (2/1) with reduced and oxidized SiO_2-supported rhodium catalysts, one can conclude that metallic rhodium is the active site for methane dissociation and syngas formation. The dissociation of methane is a key step for methane partial oxidation to syngas. In the reaction of CH_4/O_2 (2/1) over Rh/SiO_2, methane decomposition leads to the formation of CH_x ($x = 0$–3) species and the partial oxidation of CH_x would result in CO generation. The chemisorbed oxygen species are involved in the oxidation of methane. The results of deuterium isotope effect studies lead to the conclusion that both CO and CO_2 were formed via some common intermediates, viz. CH_x species ($x = 0$–3). In other words, the results of the present studies prove that the partial oxidation of methane to syngas over SiO_2-supported rhodium catalysts follows the pyrolysis mechanism under the conditions studied.

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