

CH₄/CD₄ Isotope Effect and the Mechanism of Partial Oxidation of Methane to Synthesis Gas over Rh/ γ -Al₂O₃ Catalyst

H. Y. Wang and E. Ruckenstein*

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, New York 14260

Received: July 13, 1999; In Final Form: October 29, 1999

Partial oxidation pulse experiments with CH₄/O₂ (2/1) and with CD₄/O₂ (2/1) have been carried out over the 0.05 and 1.0 wt % Rh/ γ -Al₂O₃ catalysts to determine the isotope effect of the reaction. On the basis of the results obtained for the isotope effect as a function of temperature and Rh loading, one could conclude that the mechanism of the partial oxidation of methane to synthesis gas is dependent on both metal loading and temperature. It is likely that at low loadings (e.g., 0.05 wt %), the combustion–reforming mechanism is responsible for the reaction, while at high loadings (e.g., 1.0 wt %) a combination of the combustion–reforming and pyrolysis–oxidation mechanisms is responsible at low temperatures (≤ 500 °C) and the pyrolysis–oxidation mechanism becomes dominant at high temperatures (≥ 650 °C).

1. Introduction

Currently, synthesis gas is produced industrially by the steam reforming of methane:^{1,2}



However, this process is strongly endothermic and provides a synthesis gas with too high a H₂/CO ratio for the Fischer–Tropsch and methanol syntheses. Recently, there has been renewed interest in preparing synthesis gas via the partial oxidation of methane because of the mild exothermicity of the reaction and the suitable H₂/CO ratio obtained:



The research regarding this reaction, its mechanism, and the characterization of the catalysts became one of the most active topics in catalysis.^{3–21} However, the mechanism of partial oxidation of methane to synthesis gas is still debated. Two main points of view have been suggested. Prettre et al.²² proposed a mechanism (the combustion–reforming mechanism) in which the oxidation reaction involved an initial strongly exothermic oxidation of CH₄ to CO₂ and H₂O followed by the endothermic reforming reactions of the remaining CH₄ by the H₂O and CO₂ formed in the previous step. In contrast, Schmidt et al.^{5,7,23} suggested that the synthesis gas is formed directly, without the intermediary involvement of CO₂. In their pyrolysis–oxidation mechanism, the methane pyrolysis, which constituted the first step, was followed by the surface carbon oxidation and the desorption of CO and hydrogen. Numerous researchers^{4,6,18,19,24–27} supported the combustion–reforming mechanism; there are, however, quite a few authors^{11–15,17,28} who favored the pyrolysis–oxidation mechanism. The main concern of the debate is whether CO₂ or CO is the primary product of the reaction.

To clarify the mechanism, experiments regarding the deuterium isotope effect in the partial oxidation of methane were carried out by performing CH₄ + O₂ and CD₄ + O₂ reactions

alternately in a pulse microreactor at temperatures ranging from 400 to 850 °C. The isotope effect was determined over the 0.05 and 1.0 wt % Rh/ γ -Al₂O₃ catalysts. The goal of the paper is to present the results obtained and to extract from them information about the reaction mechanism.

2. Experimental Section

2.1. Catalyst Preparation. The supported rhodium catalysts were prepared by impregnating γ -Al₂O₃ (Alfa, 60.9 m²/g) with an ethanol solution of Rh(NO₃)₃·2H₂O (Alfa); this was followed by overnight drying at 110 °C and calcination in air at 800 °C for 4 h. Rh loading means wt % Rh in the reduced catalyst.

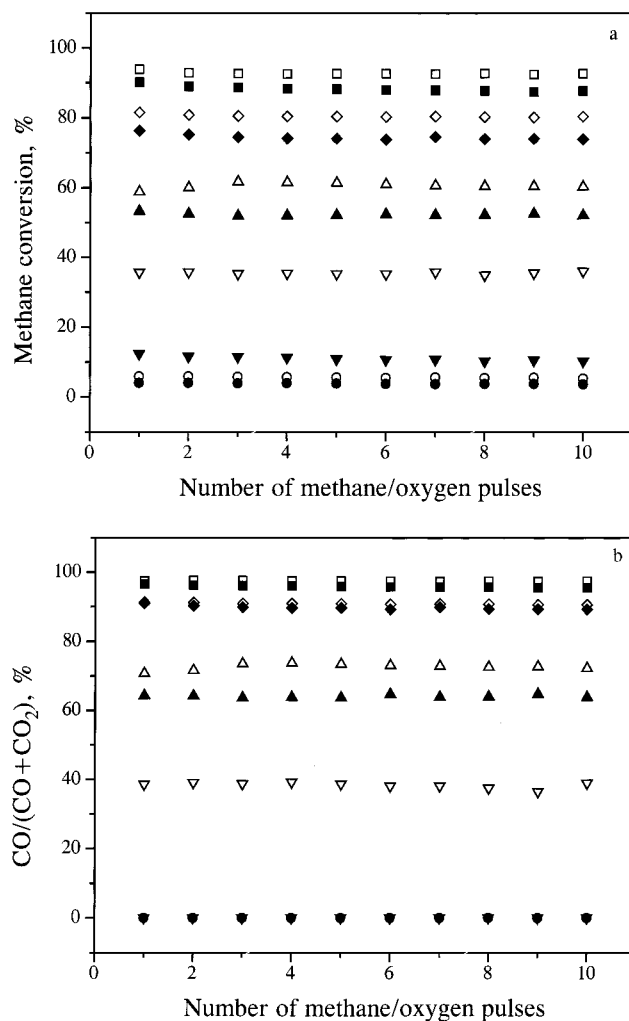
2.2. Pulse Reaction. The reaction was carried out in a pulse reaction apparatus. A vertical quartz tube (3 mm inside diameter) was used as reactor, which was operated in the down flow mode. Helium (35 mL/min), which was purified using Hydro-Purge II and Oxy-Trap columns, was employed as the carrier gas. In the pulse experiments, the reactant gas (250 μ L) was injected via a six-way sampling valve into the flowing carrier gas. The reactants and products were analyzed with an on-line gas chromatograph equipped with a thermal conductivity detector (TCD) and a Porapak Q column.

2.3. CH₄/CD₄ Isotope Effects. Five milligrams of catalyst, which was supported on quartz wool, was employed in each experiment. The catalyst was first reduced in a flow of H₂ (20 mL/min) at 600 °C for 0.5 h and then purged with a He (35 mL/min) flow for 10 min at the same temperature. After pretreatment, CH₄/O₂ (2/1) pulses were injected into the He flow to perform the CH₄ + O₂ reaction at a selected temperature, and subsequently, CD₄/O₂ (2/1) pulses were injected to perform the CD₄ + O₂ reaction at the same temperature. The conversions of methane and oxygen and yields of CO and CO₂ in the two kinds of reactions were obtained by averaging over 10 successive pulses. The time interval between two pulses of the same or different kind was 6 min. The results obtained were employed to calculate the isotope effects as the ratios of the conversion of methane, the yields of CO and CO₂ for the CH₄ + O₂ reaction to those for the CD₄ + O₂ reaction.

* To whom correspondence should be addressed.

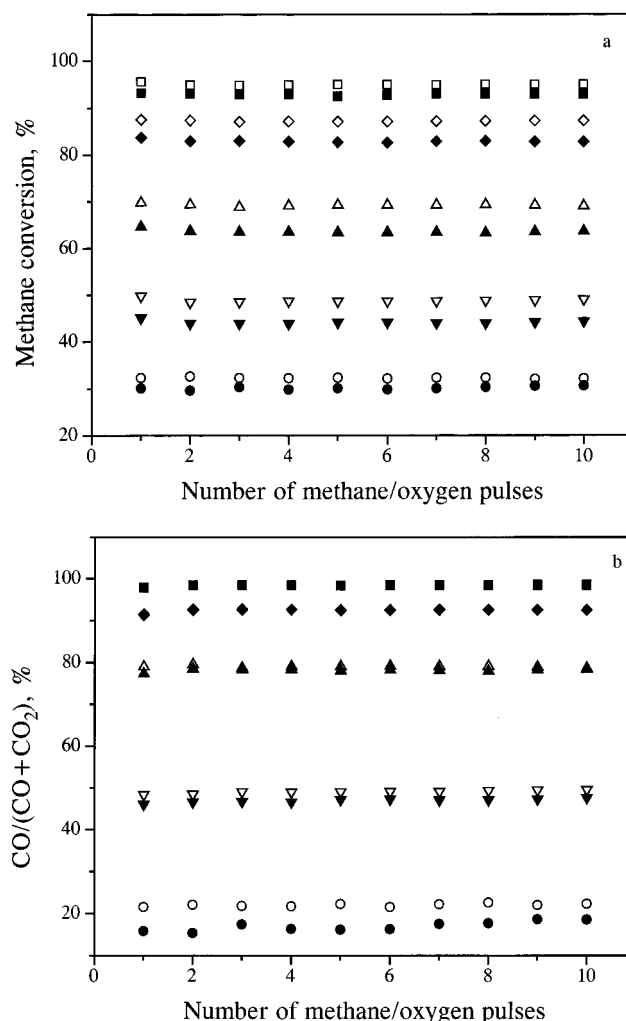
TABLE 1: Effect of Temperature on the Reactivities of CH₄/O₂ (2/1) and CD₄/O₂ (2/1) Pulses and Deuterium Isotope Effect over the 0.05 wt % Rh/ γ -Al₂O₃ Catalyst^a

temp (°C)	CH ₄ + O ₂						CD ₄ + O ₂						deuterium isotope effect		
	C _{CH₄}	C _{O₂}	S _{CO}	S _{CO₂}	Y _{CO}	Y _{CO₂}	C _{CD₄}	C _{O₂}	S _{CO}	S _{CO₂}	Y _{CO}	Y _{CO₂}	for methane conversion	for CO formation	for CO ₂ formation
450	5.52	22.83	0.00	100.00	0.00	5.52	3.80	15.87	0.00	100.00	0.00	3.80	1.45		1.45
525	31.80	100.00	26.70	73.30	8.49	23.31	9.17	36.38	0.00	100.00	0.00	9.17	3.47		2.54
550	35.04	100.00	37.38	62.62	13.10	21.94	10.60	40.90	0.00	100.00	0.00	10.60	3.31		2.07
600	39.93	100.00	46.92	53.08	18.74	21.19	35.17	100.00	36.47	63.53	12.83	22.34	1.14	1.46	0.95
650	60.91	100.00	73.04	26.96	44.49	16.42	52.17	100.00	64.06	35.94	33.42	18.75	1.17	1.33	0.88
750	80.38	100.00	90.77	9.23	72.96	7.42	74.13	100.00	89.53	10.47	66.37	7.76	1.08	1.10	0.96
850	92.56	100.00	97.38	2.62	90.13	2.43	87.96	100.00	95.73	4.27	84.21	3.75	1.05	1.07	0.65

^a C means conversion, S selectivity, and Y yield; all in percentage units.**Figure 1.** Methane conversions (a) and CO selectivities (b) in the CH₄ + O₂ (open symbols) and CD₄ + O₂ (solid symbols) reactions over the 0.05 wt % Rh/ γ -Al₂O₃ catalyst at 450 (circle), 550 (down triangle), 650 (up triangle), 750 (diamond), and 850 °C (square).

3. Results

3.1. CH₄/CD₄ Isotope Effects. The products formed during the CH₄(CD₄) + O₂ reaction contained CO, H₂(D₂), CO₂, and H₂O (D₂O). The carbon balance indicated that no carbon was deposited on the catalyst. The CH₄/CD₄ isotope effect was determined by performing the CH₄ + O₂ and CD₄ + O₂ reactions alternately at temperatures ranging from 400 to 850 °C. The results obtained over the 0.05 wt % Rh/ γ -Al₂O₃ catalyst are presented in Figure 1 and Table 1, and those over the 1.0 wt % Rh/ γ -Al₂O₃ catalyst are presented in Figure 2 and Table 2.

**Figure 2.** Methane conversions (a) and CO selectivities (b) in the CH₄ + O₂ (open symbols) and CD₄ + O₂ (solid symbols) reactions over the 1.0 wt % Rh/ γ -Al₂O₃ catalyst at 450 (circle), 550 (down triangle), 650 (up triangle), 750 (diamond), and 850 °C (square).

Over the 0.05 wt % catalyst, at 450 °C, only CO₂ was formed as a carbon-containing product in both CH₄ + O₂ and CD₄ + O₂ reactions and the conversion of oxygen was approximately 4 times that of methane (Table 1). This indicates that only complete oxidation of methane occurred at this temperature. Table 1 also shows that the rate of CO₂ formation at 450 °C for CH₄ + O₂ reaction was 1.45 times that for CD₄ + O₂. At 550 °C, CO was formed as well and O₂ was completely converted in the CH₄ + O₂ reaction but not in the CD₄ + O₂ one (Figure 1 and Table 1). In the latter reaction, the conversion of oxygen was still about 4 times that of methane, indicating the complete oxidation of CD₄. As shown in Table 1, at 550

TABLE 2: Effect of Temperature on the Reactivities of CH₄/O₂ (2/1) and CD₄/O₂ (2/1) Pulses and Deuterium Isotope Effect over the 1.0 wt % Rh/ γ -Al₂O₃ Catalyst^a

temp (°C)	CH ₄ + O ₂						CD ₄ + O ₂						deuterium isotope effect		
	C _{CH₄}	C _{O₂}	S _{CO}	S _{CO₂}	Y _{CO}	Y _{CO₂}	C _{CD₄}	C _{O₂}	S _{CO}	S _{CO₂}	Y _{CO}	Y _{CO₂}	for methane conversion	for CO formation	for CO ₂ formation
400	13.00	57.48	0.00	100.00	0.00	13.00	8.43	39.06	0.00	100.00	0.00	8.43	1.54		1.54
450	32.31	100.00	21.97	78.03	7.10	25.21	30.02	100.00	16.59	83.41	4.98	25.04	1.08	1.43	1.01
500	39.68	100.00	29.37	70.63	11.36	28.31	36.44	100.00	23.70	76.30	8.64	27.78	1.09	1.31	1.02
550	48.72	100.00	49.16	50.84	23.95	24.77	44.04	100.00	47.07	52.93	20.73	23.31	1.11	1.16	1.06
650	69.18	100.00	78.98	21.02	54.63	14.54	63.44	100.00	78.21	21.79	49.62	13.82	1.09	1.10	1.05
750	87.20	100.00	92.62	7.38	80.77	6.44	82.86	100.00	92.55	7.45	76.69	6.17	1.05	1.05	1.04
850	94.94	100.00	98.40	1.60	93.42	1.52	92.85	100.00	98.48	1.52	91.44	1.41	1.02	1.02	1.08

^a C means conversion, S selectivity, and Y yield; all in percentage units.

°C the methane conversion and CO₂ yield for the reaction involving CH₄ were 3.3 and 2.07 times, respectively, those involving CD₄. At 525 °C, the results were similar to those at 550 °C (Table 1). For temperatures of ≥ 600 °C, O₂ was completely consumed and CO was formed besides CO₂ in both cases. Both the methane conversion and the CO selectivity for the CH₄ + O₂ reaction were higher than for the CD₄ + O₂ one (Table 1 and Figure 1). With increasing reaction temperature, the difference between the CO selectivities in the two reactions became increasingly smaller; at temperatures of ≥ 750 °C, they were very close to each other (Figure 1). Regarding the isotope effect at temperatures of ≥ 600 °C, that for the CO formation decreased monotonically from 1.46 to 1.07 with an increase in the reaction temperature from 600 to 850 °C; that for the CO₂ formation was always below 1.00, and that for the methane conversion exhibited a maximum at 650 °C (Table 1).

Over the 1.0 wt % Rh/ γ -Al₂O₃ catalyst, at 400 °C, only complete oxidation of methane occurred for both CH₄ + O₂ and CD₄ + O₂ reactions, as over the 0.05 wt % catalyst at 450 °C. As shown in Table 2, at 400 °C the rate of CO₂ formation for the CH₄ + O₂ reaction was 1.54 times that for the CD₄ + O₂ reaction. At temperatures of ≥ 450 °C, O₂ was completely consumed and CO was formed besides CO₂ in both cases. The methane conversion for the CH₄ + O₂ reaction was always higher than for the CD₄ + O₂ reaction at temperatures between 450 and 850 °C (Table 2 and Figure 2). One can observe that the difference between the CO selectivities in the two reactions decreased with increasing temperature, becoming almost zero at temperatures of ≥ 650 °C (Figure 2b and Table 2). Regarding the isotope effect at temperatures of ≥ 450 °C, that for the CO formation decreased monotonically from 1.43 to 1.02 with increasing reaction temperature from 450 to 850 °C; that for the CO₂ formation was always greater than 1.00 and higher at temperatures of ≥ 550 °C than at temperatures of ≤ 500 °C, and that for the methane conversion exhibited a maximum at 550 °C (Table 2).

In summary, at temperatures of ≥ 600 °C, the isotope effects for the conversion of methane and for the CO formation were much larger over the 0.05 wt % catalyst than over the 1.0 wt % one. In addition, the deuterium isotope effect for the CO₂ formation reaction was lower than 1.00 over the 0.05 wt % catalyst but higher than 1.00 over the 1.0 wt % catalyst.

3.2. Interactions of CH₄ Pulses with the 0.05 and 1.0 wt % Rh/ γ -Al₂O₃ Catalysts. The interactions of methane pulses with the reduced 0.05 and 1.0 wt % Rh/ γ -Al₂O₃ catalysts were investigated at temperatures ranging from 550 to 850 °C. The amount of surface carbon formed in the reaction was calculated from the carbon balance. Figure 3 presents the changes of methane conversion and surface carbon (C) yield over the two catalysts as a function of the number of CH₄ pulses. Over the 0.05 wt % catalyst, only CO was detected by GC as a gaseous

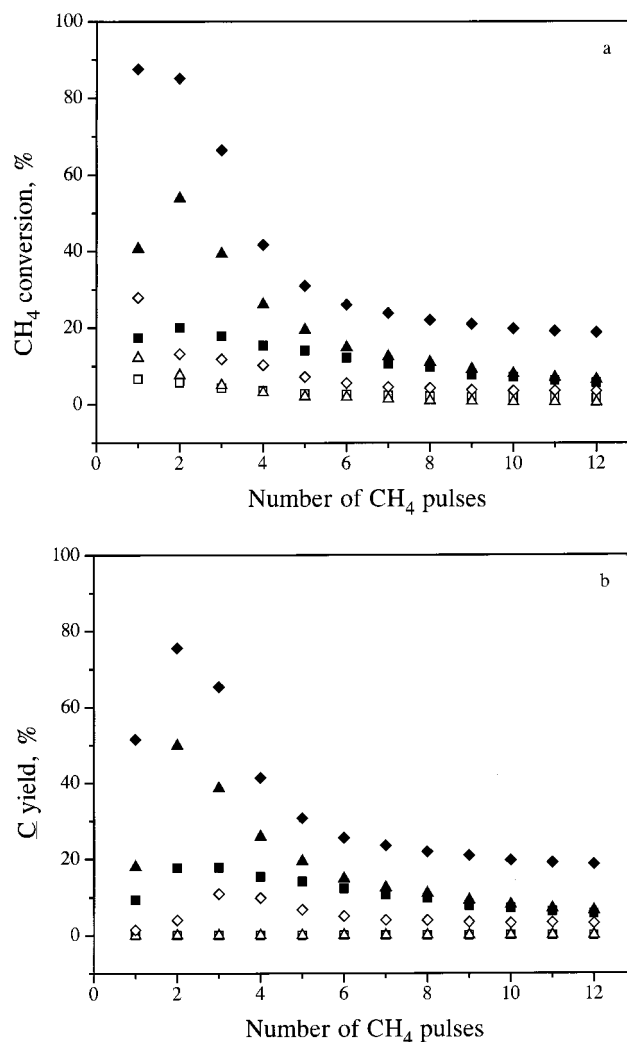


Figure 3. Methane conversions (a) and C yields (b) in the reaction of pure methane with the 0.05 (open symbols) and 1.0 (solid symbols) wt % Rh/ γ -Al₂O₃ catalysts at 550 (square), 700 (up triangle), and 850 °C (diamond). Catalyst: 50.0 mg. CH₄ pulse: 250 μ L.

carbon-containing product. Since no oxygen was present in the feed gas, the residual oxygen of the catalyst was responsible for the formation of CO. The carbon balance indicated that carbon deposition occurred to some extent at 850 °C but not at 550 and 700 °C (Figure 3b). As shown in Figure 3b, over the 0.05 wt % Rh catalyst and 850 °C, the C yield increased during the first three pulses, passed through a maximum close to 11%, and then decreased. In contrast, over the 1.0 wt % Rh catalyst, both the methane conversion and the C yield were much higher during the first six pulses than over the 0.05 wt % catalyst (Figures 3). Over the 1.0 wt % catalyst, the C yield decreased

gradually at 550 °C and more rapidly at 700 and 850 °C after passing through a maximum. The maxima of the \bar{C} yields at 550, 700, and 850 °C were 17.8, 49.8, and 75.6%, respectively. In summary, the catalyst with a 1.0 wt % Rh loading had a much stronger ability for methane dissociation than the one with 0.05 wt % loading. In addition, the rate of carbon deposition during the first six pulses increased greatly with increasing temperature over the 1.0 wt % Rh catalyst. It is clear that the coverage of the metallic rhodium sites by carbon species is responsible for the decay of methane conversion (Figure 3a).

4. Discussion

A complete conversion of oxygen and a rapid rise of the methane conversion could be regarded as a sign of ignition of the reaction. At 450 °C over the 0.05 wt % Rh catalyst and at 400 °C over the 1.0 wt % one, both the methane and oxygen conversions were relatively low (the reactions were not ignited) and only complete oxidation products, i.e., CO_2 and H_2O were formed. As shown in Tables 1 and 2, under the above conditions, the CO_2 formation reaction exhibited a noticeable deuterium isotope effect. In general, the breaking of a bond with H(D) during the rate-determining step of a reaction should provide a normal (>1) deuterium isotope effect.²⁹ Consequently, the existence of the deuterium isotope effect indicates that the rate-determining step of the reaction involves the breakage of a C–H(D) bond.

Over the 0.05 wt % catalyst, at 525 and 550 °C, Table 1 shows that the $\text{CH}_4 + \text{O}_2$ reaction was ignited while the $\text{CD}_4 + \text{O}_2$ reaction was not. Obviously, this occurs because, owing to its lower vibration frequency, CD_4 is less reactive than CH_4 . At temperatures of ≥ 600 °C, both the $\text{CH}_4 + \text{O}_2$ and $\text{CD}_4 + \text{O}_2$ reactions were ignited over the 0.05 wt % catalyst; a normal deuterium isotope effect was observed for the CO formation and the conversion of methane, but the isotope effect was below unity for the CO_2 formation. This means that the rate-determining step in the CO formation included the cleavage of a C–H(D) bond.

In summary, over the 0.05 wt % catalyst, only CO_2 was formed at 450 °C (below the ignition temperature) as a carbon-containing product from both CH_4 and CD_4 . Between 450 and 600 °C, some CO was generated in the reactions involving CH_4 but not in those involving CD_4 . As already mentioned, the former reactions but not the latter were ignited. Consequently, CO was formed only after ignition. The absence of CO below the ignition temperature is most likely due to the oxidative atmosphere caused by the incomplete consumption of O_2 . The isotope effect for the CO_2 formation was much higher between 450 and 600 °C than at 450 °C; this probably occurred because of the different temperature dependencies of the reaction rates of CH_4 and CD_4 with O_2 . The ignition temperature was between 450 and 525 °C for CH_4 and between 550 and 600 °C for CD_4 . When the reaction was carried out close to but above the ignition temperature, e.g., 525 °C for $\text{CH}_4 + \text{O}_2$ reaction and 600 °C for $\text{CD}_4 + \text{O}_2$, the CO_2 yield was below but close to 25% in both cases. These results suggest that the combustion of methane occurred with the formation of CO_2 and H_2O and that CO was formed via the reforming reactions. At temperatures greater than 600 °C, methane combustion constituted the first step with complete consumption of O_2 in both cases. Because the reaction is oxygen-limited, only 25% of methane (CH_4 or CD_4) was converted and equal amounts of CO_2 were formed in the first step in both cases. In the second step, CO was generated through the reforming of methane by the CO_2 and H_2O formed in the first step. Because of the normal deuterium isotope effect, more

CO was formed and more CO_2 consumed in the reaction involving CH_4 than CD_4 . As a result, more CO_2 remained in the $\text{CD}_4 + \text{O}_2$ reaction and the isotope effect for CO_2 formation became less than 1.00 (Table 1). The combustion of methane is much faster than the CO_2 and H_2O reforming of methane. Therefore, the reaction rate for CO formation was controlled by the cleavage of a C–H(D) bond that occurred during the reforming process. The yield of CO became dominant at temperatures greater than 650 °C because the rates of the reforming reactions increase rapidly with temperature.

The 1.0 wt % Rh catalyst had a lower ignition temperature than the 0.05 wt % one. Over the former catalyst, at temperatures of ≥ 450 °C, both reactions were ignited. Compared to the 0.05 wt % catalyst, a smaller normal deuterium isotope effect for the CO formation was observed over the 1.0 wt % catalyst. While the isotope effect for the CO_2 formation was always below 1.00 over the 0.05 wt % catalyst, it was always above 1.00 over the 1.0 wt % catalyst and higher at temperatures of ≥ 550 °C than at temperatures of ≤ 500 °C. We suggest that the reaction involves the two mechanisms (combustion–reforming and pyrolysis–oxidation) occurring simultaneously at low temperatures (≤ 500 °C) and that the pyrolysis–oxidation mechanism is dominant at high temperatures (≥ 650 °C). Indeed, at low temperatures (≤ 500 °C), the isotope effects for the CO and CO_2 formation reactions were very different and an isotope effect above unity was observed for the CO_2 formation (Table 2). In the pyrolysis–oxidation mechanism, the CO and CO_2 originate from the same carbon-containing species, CH_x ($x = 0-3$), and consequently, comparable normal isotope effects (>1.00) are expected for CO and CO_2 . Since the two isotope effects are very different at temperatures below 500 °C, it is likely that the pyrolysis–oxidation mechanism is not (or is not alone) responsible for the reaction. Similarly, the combustion–reforming mechanism cannot alone explain the experimental results because this mechanism would lead to an isotope effect smaller than unity for CO_2 . However, the pyrolysis–oxidation mechanism can provide a deuterium isotope effect for CO_2 greater than unity and the combustion–reforming can provide different values for the isotope effects for CO and CO_2 . Consequently, a combination of the two mechanisms is compatible with the experimental results. In addition, Table 2 shows that, particularly at 500 °C, the yield of CO_2 is greater than 25%. This implies that an additional pathway for the formation of CO_2 (e.g., CO oxidation) was present besides combustion. Therefore, it is likely that both mechanisms played a role at low temperatures. At high temperatures (≥ 650 °C), the isotope effects for CO and CO_2 were similar to each another and the CO selectivities were almost the same in both reactions (Table 2 and Figure 2b); consequently, the experimental results are compatible with the pyrolysis–oxidation mechanism. A similar result for the 0.5 wt % Rh/ SiO_2 catalyst at 700 °C was also reported.¹⁷ An additional argument for this mechanism is as follows. In the pyrolysis–oxidation mechanism, the CO and CO_2 selectivities are mainly determined by the following two competitive reactions: (i) the desorption of CO_s to CO_g , (ii) the oxidation of CO_s to $\text{CO}_{2,s}$ and desorption of $\text{CO}_{2,s}$. The rates of CO_s desorption to CO_g and of its further oxidation to $\text{CO}_{2,s}$ and desorption are free of any deuterium isotope effect. For this reason, the same product selectivity should occur in both $\text{CH}_4 + \text{O}_2$ and $\text{CD}_4 + \text{O}_2$ reactions. Figure 2b shows that at high temperatures (≥ 650 °C), the CO selectivities are almost the same in both cases. This strengthens the conclusion that the pyrolysis–oxidation mechanism is mainly responsible for the partial oxidation reaction over the 1.0 wt % catalyst at high

temperatures. At low temperatures, the combustion—reforming mechanism also plays a role, and for that reason, the selectivities are no longer equal (Figure 2b and Table 2).

The experiments carried out with CH₄ pulses also provide some insight into the mechanism of the partial oxidation of methane. Indeed, in the reaction of pure methane with the reduced 0.05 and 1.0 wt % Rh catalysts, a noticeable amount of carbon was deposited at temperatures between 550 and 850 °C over the latter catalyst but not over the former catalyst. Of course, the generation of surface carbon from pure methane over the metallic rhodium sites follows a direct pyrolysis mechanism: CH_{4,s} → CH_{x,s} → C_s. Because no carbon was deposited over the 0.05 wt % catalyst, it is unlikely that the pyrolysis—oxidation mechanism played a major role over that catalyst. In contrast, carbon depositions occurred over the 1.0 wt % Rh catalyst, and this indicates that the pyrolysis—oxidation mechanism might have played a role in that case. Because at temperatures below 550 °C only relatively small amounts were deposited upon the 1.0 wt % catalyst, while at higher temperatures the amounts deposited were much higher, the role of the latter mechanism is expected to be greater at higher than at lower temperatures. These conclusions are in agreement with those revealed by the isotope experiments.

5. Conclusion

Pulse isotope effect experiments for the partial oxidation of CH₄ (CD₄) to synthesis gas over Rh/γ-Al₂O₃ catalysts as well as CH₄ pulse experiments over the same catalysts revealed that the mechanism of oxidation is dependent on the loading of the catalyst and the reaction temperature. It is likely that at low loadings (0.05 wt % Rh) a combustion—reforming mechanism is responsible for the reaction, while at high loadings (1.0 wt % Rh) a combination of the combustion—reforming and pyrolysis—oxidation mechanisms is responsible at low temperatures and the pyrolysis—oxidation constitutes the main mechanism at high temperatures.

References and Notes

- (1) Trimm, D. L. *Catal. Rev. Sci. Eng.* **1977**, *16*, 155.
- (2) Rostrup-Nielsen, J. R. *Catal. Today* **1993**, *18*, 305.
- (3) Ashcroft, A. T.; Cheetham, A. K.; Foord, J. S.; et al. *Nature* **1990**, *344*, 319.
- (4) Dissanayake, D.; Rosynek, M. P.; Kharas, K. C. C.; Lunsford, L. H. *J. Catal.* **1991**, *132*, 117.
- (5) Hickman, D. A.; Schmidt, L. D. *J. Catal.* **1992**, *138*, 267.
- (6) Dissanayake, D.; Rosynek, M. P.; Lunsford, L. H. *J. Phys. Chem.* **1993**, *97*, 3644.
- (7) Hickman, D. A.; Schmidt, L. D. *Science* **1993**, *259*, 343.
- (8) Tornaiainen, P. M.; Chu, X.; Schmidt, L. D. *J. Catal.* **1994**, *146*, 1.
- (9) Buyevskaya, O. V.; Wolf, D.; Baerns, M. *Catal. Lett.* **1994**, *29*, 249.
- (10) Slagtern, A.; Olsbye, U.; *Appl. Catal. A* **1994**, *110*, 99.
- (11) Hu, Y. H.; Ruckenstein, E. *Catal. Lett.* **1995**, *34*, 41.
- (12) Hu, Y. H.; Ruckenstein, E. *J. Catal.* **1996**, *158*, 260.
- (13) Au, C. T.; Wang, H. Y.; Wan, H. L. *J. Catal.* **1996**, *158*, 343.
- (14) Choudhary, V. R.; Uphade, B. S.; Belhekar, A. A. *J. Catal.* **1996**, *163*, 312.
- (15) Mallens, E. P. J.; Hoebink, J. H. B. J.; Marin, G. B. *J. Catal.* **1997**, *167*, 43.
- (16) Lago, R.; Bini, G.; Pena, M. A.; J. Fierro, L. G. *J. Catal.* **1997**, *167*, 198.
- (17) Au, C. T.; Wang, H. Y. *J. Catal.* **1997**, *167*, 337.
- (18) Looij, F. van; Geus, J. W. *J. Catal.* **1997**, *168*, 154.
- (19) Tsipourari, V. A.; Zhang, Z.; Verykios, X. E. *J. Catal.* **1998**, *179*, 283.
- (20) Tsipourari, V. A.; Verykios, X. E. *J. Catal.* **1998**, *179*, 292.
- (21) Wang, H. Y.; Ruckenstein, E. *J. Catal.* **1999**, *186*, 181.
- (22) Prettre, M.; Eichner, C.; Perrin, M. *Trans. Faraday Soc.* **1946**, *42*, 335.
- (23) Hickman, D. A.; Hauofear, E. A.; Schmidt, L. D. *Catal. Lett.* **1993**, *17*, 223.
- (24) Vernon, P. D. F.; Green, M. L. H.; Cheetham, A. K.; Ashcroft, A. T. *Catal. Lett.* **1990**, *6*, 181.
- (25) Chang, Y. F.; Heinemann, H. *Catal. Lett.* **1993**, *21*, 215.
- (26) Matsumura, Y.; Moffat, J. B. *Catal. Lett.* **1994**, *24*, 59.
- (27) Nakagawa, K.; Anzai, K.; Matsui, N.; et al. *Catal. Lett.* **1998**, *51*, 163.
- (28) Wang, D.; Dewaele, O.; Groote, A. M. De; Froment, G. F. *J. Catal.* **1996**, *159*, 418.
- (29) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.