Pulse-MS studies on CH_4/CD_4 isotope effect in the partial oxidation of methane to syngas over Pt/α-Al_2O_3

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By replacing $CH_4 + O_2$ with $CD_4 + O_2$, the deuterium isotope effect in the partial oxidation of methane over Pt/α-Al_2O_3 was studied in the temperature range of 550–650 °C using the pulse-MS method. The effect of space velocity of carrier gas and CO_2 reforming of CH_4 to syngas were also investigated. No deuterium isotope effect was observed for CH_4 conversion whereas CO formation showed a normal deuterium isotope effect. The surface reaction between adsorbed hydrocarbon species and adsorbed oxygen species to CO formation may be a relatively slow step. The results support the parallel mechanism, namely CO and CO_2 are simultaneously formed in parallel from the direct oxidation of methane.

Keywords: pulse-MS, partial oxidation of methane, deuterium isotope effect, Pt/α-Al_2O_3

1. Introduction

Recently renewed attention has been focused onto the partial oxidation of methane (POM) to syngas due to its potential advantages over conventional steam reforming of methane to syngas [1–4]: (i) POM produces syngas with low H_2/CO ratio ($H_2/CO \approx 2$) suitable for methanol synthesis or Fischer–Tropsch process; (ii) POM reaction is slightly exothermic and thus would be much more energy-efficient than steam reforming of methane which is highly endothermic; (iii) smaller reactors (or higher throughput) would be possible because high methane conversion and selectivities to CO and H_2 may be achieved by POM in short contact time ($\leqslant 10^{-2}$ s) [5].

The reaction mechanism of the partial oxidation of methane to syngas is a subject of intensive studies but still of controversies. Several authors [6–8] have pointed out that POM over a variety of catalysts involves complete oxidation of methane to CO_2 and H_2O and subsequent reforming reaction of the residual CH_4 with CO_2 and H_2O. This "indirect reaction scheme" can explain the presence of severe hot spots and steep temperature gradients, especially at the entrance of the catalyst bed. The "indirect reaction scheme" may also include the reverse Boudouard reaction, in which CO is formed via a fast reaction of surface carbon and CO_2 [9]. However, other authors [10–12] have claimed that CO and H_2 are directly formed as primary reaction products while CO_2 is produced by further oxidation of CO. Besides, parallel formation of CO and CO_2 for the partial oxidation of methane has also been suggested over transition metals supported on metal oxides [13,14].

In regard to the elucidation of the reaction mechanism, measuring the isotope effect is informative [15,16]. In the present paper, the CH_4/CD_4 isotope effect in POM has been investigated by pulse-MS, the use of which will eliminate hot spots in the catalyst bed because of the very small amount of reactants in a pulse.

2. Experimental

0.25 wt% Pt/α-Al_2O_3 catalyst was prepared by incipient wetness impregnation of α-Al_2O_3 powder (Johnson Matthey) with a dilute hydrochloric acid solution of $PtCl_4$ (Merck). After impregnation, the catalyst was dried in air and then calcined for 4 h at 600 °C.

A quartz tube reactor (I.D. 4 mm) was charged with 25 mg of the catalyst (2 mm in height), with particle size of 0.3–0.5 mm. The catalyst was reduced in hydrogen at 550 °C for 30 min and then purged by ultra-high purified helium for 20 min. Ultra-high purified helium was also used as the carrier gas at a flow rate of 100 ml/min, unless specified otherwise. The reactant gas mixture was flushed onto the catalyst via carrier gas and the volume of each pulse was 1 ml. Many pulses of $CH_4 + O_2$ ($CH_4/O_2 = 2$) were first admitted for the fresh catalyst to reach a steady state. Then $CD_4 + O_2$ ($CD_4/O_2 = 2$) was pulsed 10–12 times, and $CH_4 + O_2$ was flushed again. The time interval between pulses during the $CH_4 + O_2$ or $CD_4 + O_2$ reaction was 2.5 min while it was 5 min during the alternation process between $CH_4 + O_2$ and $CD_4 + O_2$. The premixed reactant gases employed were 20% CD_4/10% O_2/He (Cambridge Isotope Lab.), 20% CH_4/10% O_2/He and 20% CH_4/20% CO_2/He (Singapore Oxygen Air Liquid).

The effluent gases were monitored with an on-line mass spectrometer (Balzers QMS 421) equipped with fast response inlet capillary system. For mass spectroscopic identification of the different compounds, the following

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atomic mass units (AMU) were used: 2 (H_2); 4 (He, D_2); 16 (CH_4); 18 (H_2O, CD_4); 20 (CD_4, D_2O); 28 (CO); 32 (O_2); 44 (CO_2). D_2 and D_2O cannot be identified by MS because their AMU are the same as He and CD_4, respectively. The mass spectrometer was calibrated with a gas mixture of known composition and calibration factors were obtained. A correction was also made for the contribution of CO_2 to AMU = 28 from its signal at AMU = 44. Methane conversion was defined as $X_{\mathrm{CH_4}}$ (mol%) $= (n_{\mathrm{in.CH_4}} - n_{\mathrm{out.CH_4}})/n_{\mathrm{in.CH_4}}$, where n is the total amount of moles, and CO selectivity (S_{CO}, mol%) was calculated on the basis of carbon contents in the products. CO yield was defined as Y_{CO} (mol%) $= X_{\mathrm{CH_4}} S_{\mathrm{CO}}$. This calculation was reliable since no carbon deposit and C_2 products were detected. In order to decrease the random error of pulse experiments, the data for the CH_4/CD_4 conversion, CO selectivity and CO yield were taken from the average of 8–10 pulses. To investigate the isotope effect the methane conversion, CO selectivity and CO yield were compared between the $CH_4 + O_2$ and $CD_4 + O_2$ reactions.

3. Results and discussion

The CH_4/CD_4 conversion, CO selectivity and CO yield at 550 and 650 °C, measured as described in the experimental section, are shown in figure 1. Upon the replacement of $CH_4 + O_2$ by $CD_4 + O_2$, CD_4 conversion is almost the same as the CH_4 conversion (figure 1(a)). However, CO selectivity and CO yield, namely the formation of CO, decrease noticeably, especially at 550 °C (figure 1 (b) and (c)). Though not shown, CO_2 selectivity and yield increase accordingly. When $CD_4 + O_2$ is alternated to $CH_4 + O_2$ again, CH_4 conversion, CO selectivity and CO yield recover. Similar trends were observed at 575, 600 and 625 °C, as summarized in table 1. The ratio of CO yield from $CH_4 + O_2$ vs. $CD_4 + O_2$, $Y^{\mathrm{H}}_{\mathrm{CO}}/Y^{\mathrm{D}}_{\mathrm{CO}}$, increases with the decrease of reaction temperature, with 1.28 at 550 °C and 1.04 at 650 °C. It should be mentioned that in all cases oxygen was completely consumed. These results indicate that the CH_4 conversion does not show a deuterium isotope effect whereas CO formation does. As will be discussed in more details later, this appears to suggest that the surface reaction between adsorbed hydrocarbon species and adsorbed oxygen species, rather than the dissociative adsorption of CH_4, is a rate-determining step in POM. This is in agreement with Osaki et al.'s results [16] that for CO_2 reforming of CH_4 the reaction of adsorbed hydrocarbon species with CO_2 (or adsorbed oxygen atoms) is rate-controlling. In addition, the results that CH_4 conversion and CO selectivity rise with the increase of reaction temperature (table 1) are consistent with the trends predicted by thermodynamic equilibrium calculation [17]. At elevated temperature, equilibrium predicts a greater conversion of methane and greater syngas formation from a mixture of methane and oxygen.

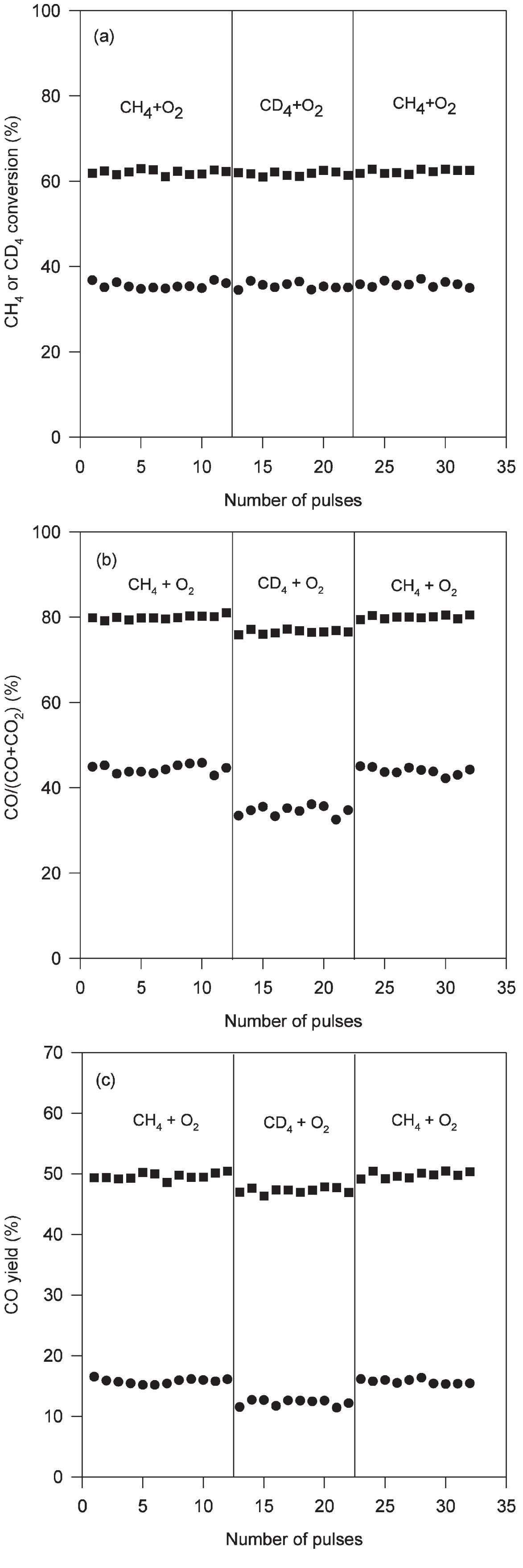


Figure 1. (a) CH_4/CD_4 conversion, (b) CO selectivity and (c) CO yield vs. number of pulses: (●) 550 °C, (■) 650 °C.

Table 1
The comparison of CH_4/CD_4 conversion, CO selectivity and CO yield between the $CH_4 + O_2$ and $CD_4 + O_2$ reactions at several reaction temperatures (flow rate of He, 100 ml/min).

Temperature	$CH_4 + O_2$			$CD_4 + O_2$			Ratio of
(°C)	X_{CH_4}	S_{CO}	Y^H_{CO}	X_{CD_4}	S_{CO}	Y^D_{CO}	Y^H_{CO}/Y^D_{CO}
550	35.6	44.5	15.8	35.5	34.6	12.3	1.28
575	44.9	57.1	25.6	45.0	50.3	22.6	1.13
600	50.1	64.5	32.3	49.5	59.6	29.5	1.09
625	57.2	73.8	42.2	57.3	69.9	40.0	1.06
650	61.9	79.9	49.4	61.7	76.6	47.3	1.04

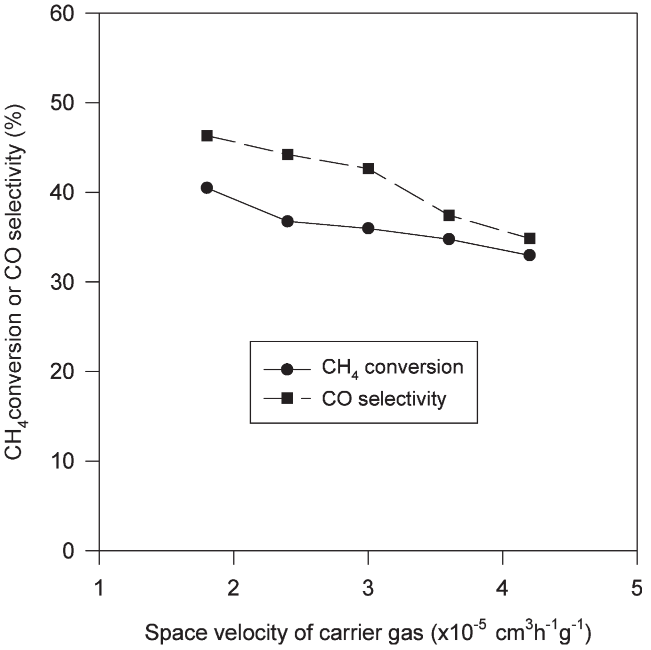


Figure 2. The effect of space velocity of carrier gas on CH_4 conversion and CO selectivity under pulse condition at 550 °C: flow rate of carrier gas from 75 to 175 ml/min; feed gases, 20% CH_4/10% O_2/He.

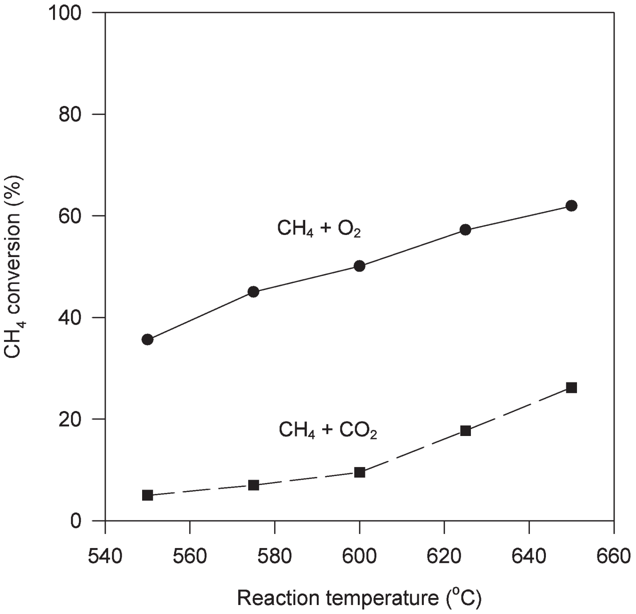
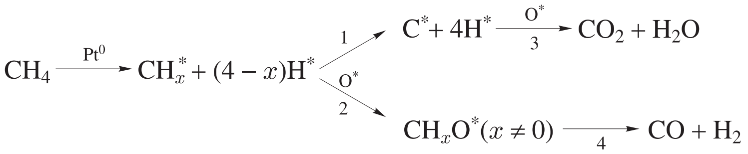


Figure 3. The comparison of CH_4 conversion between the partial oxidation of methane and CO_2 reforming of methane to syngas under pulse condition at the same space velocity of carrier gas (He, 100 ml/min): feed gases, (●) 20% CH_4/10% O_2/He; (■) 20% CH_4/20% CO_2/He.

Figure 2 illustrates the effect of space velocity of carrier gas on the CH_4 conversion and CO selectivity at 550 °C. As the space velocity of carrier gas increases from 1.8×10^5 to 4.2×10^5 $cm^3\,h^{-1}\,g^{-1}$, both CH_4 conversion and CO selectivity gradually decrease. These results, which were obtained from pulse experiments, contradict with those under continuous flow conditions reported by Choudhary et al. [18]. They observed that the CH_4 conversion and CO selectivity both increased with the increase of space velocity of feed gases ($CH_4/O_2 = 2$) without diluents. As pointed out by Chang and Heinemann [19], Choudhary's results may be incorrect, affected by harsh hot spots in the catalyst bed. From the view of thermodynamic equilibrium, by allowing more contact time at high temperature the reaction mixture could be heading towards equilibrium composition. The long contact time (low space velocity) is thus beneficial for the formation of CO if the harsh hot spots do not exist in the catalyst bed. In general, if CO_2 is predominantly formed by the consecutive oxidation of CO, CO selectivity should decrease with the increase of the contact time. Therefore, the observation in figure 2 where CO selectivity decreases with decrease of the contact time seems to imply that CO_2 is not mainly formed by the further oxidation of CO.

Figure 3 contrasts CH_4 conversion of $CH_4 + O_2$ to syngas with that of $CH_4 + CO_2$ reforming reaction under similar reaction conditions. At lower temperatures ($\leqslant$600 °C) CH_4 conversion for $CH_4 + CO_2$ reforming is very low. However, with increasing reaction temperature (>600 °C), it increases largely (9.5% at 600 °C and 26.2% at 650 °C).

The above results cannot be explained based on the "indirect reaction scheme", i.e., CO is produced not directly from $CH_4 + O_2$, but from $CH_4 + CO_2$ and $CH_4 + H_2O$. Recently, Wang and Au [20] studied the CH_4/CD_4 isotope effect in the $CH_4 + CO_2$ reforming reaction over Ni/SiO_2 by using pulse-MS. It was found that CH_4 conversion was obviously larger than CD_4 conversion at 700 °C, showing a normal deuterium isotope effect for $CH_4 + CO_2$. On the other hand, Ross and Steel [21] have investigated the exchange reaction of $CH_4 + D_2O$ and $CH_4 + H_2O + D_2$ over Ni/Al_2O_3, and confirmed the often quoted assumption that the dissociative adsorption of CH_4 is the rate-controlling step for $CH_4 + H_2O$. Our results are obviously different from those of Wang–Au and Ross–Steel since in our study



Scheme 1.

CH_4 conversion was almost the same as the CD_4 conversion. These contradict with the “indirect mechanism”, indicating that CO_2 and steam reforming of residual CH_4 are not the main reaction paths for our system. This conclusion is also supported by the data illustrated in figure 3, where CH_4 conversion for CO_2 reforming of methane is much lower than that for partial oxidation of methane. Actually, our results can be resonably explained based on the proposed parallel mechanism in scheme 1.

CH_4 is firstly dissociated to produce adsorbed CH_x species on metal Pt surfaces. The CH_x species will then react with surface adsorbed oxygen to form CO and CO_2 through two different suface reaction routes which compete with each other. CO is formed through the CH_xO^* intermediate species (steps $2 + 4$) while CO_2 is produced through the complete dehydrogenation (step 1) and the subsequent oxidation reaction of surface carbon species (step 3). The dissociative adsorption of methane is a fast step since no deuterium isotope effect of CH_4 conversion has been observed (table 1). When $CH_4 + O_2$ is replaced by $CD_4 + O_2$, the yield of CO through route $2 + 4$ decreases if the reaction involving CH_x ($x \neq 0$) and adsorbed oxygen is a slow step. In this case the surface concentration of adsorbed CH_x species and adsorbed oxygen species may increase, then CH_x will further dissociate to produce more surface carbon species through route 1, leading to the production of more CO_2 through reaction route 3. As a result, CO yield decreases but CD_4 conversion remains almost unchanged for the $CD_4 + O_2$ reaction. Since the complete dissociation of CH_x of step 1 is assumed to be a relatively fast step and no CH_x is involved in the formation of CO_2 in step 3, CO_2 formation does not show the normal deuterium isotope effect. This parallel reaction scheme can find support from literature. Wang et al. [22] studied the partial oxidation of methane to syngas over Rh/Al_2O_3 using temporal analysis of products (TAP) and found that the products and the kinetics of oxidation of CH_4 depended on the concentration of adsorbed oxygen. At high concentrations of adsorbed oxygen, the primary products were H_2O and CO_2 whereas at low concentrations of adsorbed oxygen, the primary products were CO and H_2. In view of the large difference between the rates of CO and CO_2 formation, we reckon that CO_2 and CO are formed through different adsorbed oxygen species. Recently, Puglia et al. [23] observed two types of chemisorbed molecular oxygen (superoxo-like and peroxo-like configuration) as well as an atomic oxygen phase on Pt(111). Nevertheless, different surface species may convert to one another and reach an equilibrium. Further investigation is necessary for identification of these surface species.

It should be mentioned that the partial oxidation of methane to syngas is a complicated process. It cannot be excluded that CO may be also formed by the secondary reformings of methane, especially at higher temperature ($\geqslant$650 °C). However, we think CO is mainly formed by the direct route as explained above based on the results of the CH_4/CD_4 isotope effect.

In summary, the studies of CH_4/CD_4 isotope effect and space velocity effect suggest that the surface reaction between adsorbed hydrocarbon species and adsorbed oxygen species to form CO is relatively slow. CO and CO_2 are simultaneously produced in parallel through different reaction routes.

References

[1] R. Lago, G. Bini, M.A. Pena and J.L.G. Fierro, J. Catal. 167 (1997) 198.
[2] N. Nichio, M. Casella, O. Ferretti, M. Gonzalez, C. Nicot, B. Moraweck and R. Frety, Catal. Lett. 42 (1996) 65.
[3] A.A. Lemonidou, A.E. Stabouli, G.J. Tjatjopoulos and I.A. Vasalos, Catal. Lett. 43 (1997) 235.
[4] S. Tang, J. Lin and K.L. Tan, Catal. Lett. 51 (1998) 169.
[5] D.A. Hickman, E.A. Haupfear and L.D. Schmidt, Catal. Lett. 17 (1993) 223.
[6] D. Dissanayake, M.P. Rosynek, K.C.C. Kharas and J.H. Lunsford, J. Catal. 132 (1991) 117.
[7] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell and P.D.F. Vernon, Nature 344 (1990) 319.
[8] F.V. Looij, J.C.V. Giezen, E.R. Stobbe and J.W. Geus, Catal. Today 21 (1994) 495.
[9] O.V. Buyevskaya, K. Walter, D. Wolf and M. Baerns, Catal. Lett. 38 (1996) 81.
[10] V.R. Choudhary, A.M. Rajput and B. Prabhakar, J. Catal. 139 (1993) 326.
[11] D.A. Hickman and L.D. Schmidt, Science 259 (1993) 243.
[12] E.P.J. Mallens, J.H.B.J. Hoebink and G.B. Marin, J. Catal. 167 (1997) 43.
[13] J.A. Lapszewicz and X.-Z. Jiang, Prepr. Am. Chem. Soc. Div. Petrol. Chem. 37 (1992) 252.
[14] Y. Matsumura and J.B. Moffat, Catal. Lett. 24 (1994) 59.
[15] H. Kato, C. Yokoyama and M. Miaono, Catal. Lett. 47 (1997) 189.
[16] T. Osaki, T. Horiuchi, K. Suzuki and T. Mori, Catal. Lett. 44 (1997) 19.
[17] S.C. Tsang, J.B. Claridge and M.L.H. Green, Catal. Today 23 (1995) 3.
[18] V.R. Choudhary, A.M. Rajput and B. Prabhakar, Catal. Lett. 15 (1992) 363.
[19] Y.F. Chang and H. Heinemann, Catal. Lett. 21 (1993) 215.
[20] H.Y. Wang and C.T. Au, Catal. Lett. 38 (1996) 77.
[21] J.R.H. Ross and M.C.F. Steel, J. Chem. Soc. Faraday Trans. I 69 (1973) 10.
[22] D. Wang, O. Dewaele, A.M.D. Groote and G.F. Froment, J. Catal. 159 (1996) 418.
[23] S. Jentz, M. Trenary, X.D. Peng and P. Stair, Surf. Sci. 341 (1995) 282.