Pulse-MS study of the partial oxidation of methane over Ni/La_2O_3 catalyst

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Received 7 March 1995; accepted 30 April 1995

The CH_4 direct oxidation reaction was studied at 600°C by the pulse-MS transient method over the Ni/La_2O_3 catalyst. Over the freshly prepared catalyst (which contains NiO), the CO selectivity and CH_4 conversion increased and attained constant values as the number of CH_4/O_2 pulses increased. Over the reduced catalyst (containing Ni), as the number of CH_4/O_2 pulses increased, the CO selectivity and CH_4 conversion decreased before they reached the same constant values as over the fresh catalyst. The CO selectivity increased as the residence time of the reactants shortened, implying that CO was directly generated without the preformation of CO_2. The activation energies of CH_4 dehydrogenation in the presence and absence of oxygen have been calculated using the bond-order conservation Morse-potential approach. The results indicate (1) the direct dehydrogenation steps are more likely to occur; (2) the transient oxygen species adsorbed on-top of the metal atoms promote dehydrogenation; (3) the oxygen species adsorbed on bridge or hollow sites do not promote dehydrogenation.

Keywords: methane oxidation; MS; nickel; lanthanum

1. Introduction

During the last decade, the attempts to convert methane directly into more valuable chemicals have focused on the oxidative coupling [1,2], which yields ethylene (or ethane), and on direct oxygenation, which produces methanol, or formaldehyde [3,4]. Unfortunately, these reactions have low yields of useful products and, therefore, cannot be employed at industrial scale. For this reason, in recent years, there has been renewed interest in the catalytic oxidation of CH_4 to syngas [5–12]:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \quad \Delta H = -22.6\,\text{kJ/mol}. \tag{1}$$

This reaction is mildly exothermic and provides a molar ratio H_2/CO of 2 : 1, which can be directly used as feed for the Fischer–Tropsch synthesis and methanol synthesis.

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The dominant commercial method employed to produce the synthesis gas is the steam reforming of hydrocarbons, which produces from methane a H_2/CO ratio of 3/1 [13,14],

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H = 225.4\,\text{kJ/mol}. \tag{2}$$

This reaction is endothermic, and typical reaction conditions for a Ni/Al_2O_3 catalyst are 15–30 atm and 850–900°C.

Compared to the steam reforming reaction, the direct oxidation reaction is much more energy efficient, more selective and can produce a better H_2/CO ratio. Very recently, high selectivities for CO and H_2 with excellent methane conversion over a series of catalysts have been reported [8–12,15–16]. Particularly two research groups have independently developed a new process for the oxidative methane conversion to synthesis gas [7–10,15]. The process is characterized by very short contact times between the reactants (methane and oxygen) and the catalyst. Schmidt and coworkers used catalysts containing platinum or rhodium and a temperature at the reactor exit of approximately 1000°C [7,8]. Choudhary and coworkers employed catalysts containing nickel or cobalt and reported that the reaction could take place at temperatures between 300 and 700°C and that the CO selectivity was higher than that corresponding to equilibrium [10]. However, Dissanayake et al. have suggested recently that the high selectivities obtained by Choudhary et al. might have been caused by undetected hot spots. Indeed, the temperature of a hot spot can be as much as 300°C greater than that in its immediate neighborhood in the catalyst bed [17].

In 1946, Prettre et al. [18] studied the above reaction over a nickel catalyst and concluded that the overall direct oxidation involves an initial very exothermic oxidation of CH_4 to CO_2 and H_2O, followed by the endothermic reactions (2) and (3)

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2, \quad \Delta H_{1000\,K} = 260.5\,\text{kJ/mol}. \tag{3}$$

While some recent investigations [5,6,17] concurred with the above mechanism, others [7–12] suggested that methane oxidation to synthesis gas occurs directly, without the preformation of CO_2.

In the present paper, we have employed a pulse-MS system to study the methane oxidation to syngas over Ni/La_2O_3 at the low temperature of 600°C. Because of the very small amount of feed involved in a pulse, this procedure eliminates the danger of hot spots. The on-line mass spectrometer employed also provides a highly sensitive response to products.

2. Experimental

2.1. CATALYST PREPARATION

The Ni/La_2O_3 catalyst (containing 20 wt% nickel) was prepared by impregnating La_2O_3 powder (Aldrich) with a nickel nitrate (Alfa) solution. The paste gener-

ated was dried at 110°C in air, then decomposed at 500°C and calcined at 800°C in O_2 (20 ml/min) for 4 h.

2.2. PULSE-MS

A quartz tube (2 mm inside diameter) was used as reactor. The catalyst powder (weight: 0.02 g, bed height: 2 mm) was held on quartz wool. The reactant composition was CH_4/O_2 (2/1) and the pulse volume was 0.90 ml. Ultrahigh purity helium was used as carrier gas, with a flow rate of 100 ml/min (GHSV: 300000 $cm^3\ g^{-1}\ h^{-1}$), unless otherwise stated. The analysis of gases during the transients was carried out with an on-line mass spectrometer (HP Quadrupole, 5971 Series Mass Selective Detector) equipped with a fast response inlet capillary system (fig. 1). The calibration of the mass spectrometer was performed with prepared mixtures of known composition. The cracking coefficients of methane, CO and CO_2 have been determined and used to calculate their concentrations.

2.3. BOND-ORDER CONSERVATION MORSE-POTENTIAL (BOC-MP) CALCULATION

The BOC-MP procedure, developed by Shustorovich et al. [19–21], was employed to evaluate the activation energies for the elemental steps of CH_4 dissociation in the presence and absence of three kinds of chemisorbed oxygen (on-top, bridge and hollow sites) on Ni(100) and Ni(111). The chemisorption heats of atomic carbon, hydrogen and oxygen needed in the calculations were taken from ref. [19] (for details see appendix).

3. Results

3.1. EFFECT OF THE CATALYST STATE ON METHANE OXIDATION

The selectivities and conversions were determined as a function of the number of CH_4/O_2 pulses by the pulse-MS method. Fig. 2 provides the CH_4 conversion as a

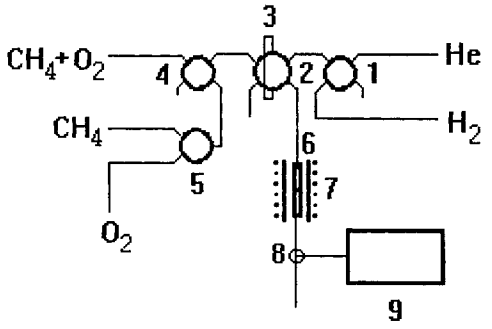

Fig. 1. Schematic diagram of the pulse-MS system. (1 and 4: four-way valves; 2: six-way valve; 3: sampling tube; 5: three-way valve; 6: reactor; 7: electronic oven; 8: split; 9: mass selective detector)

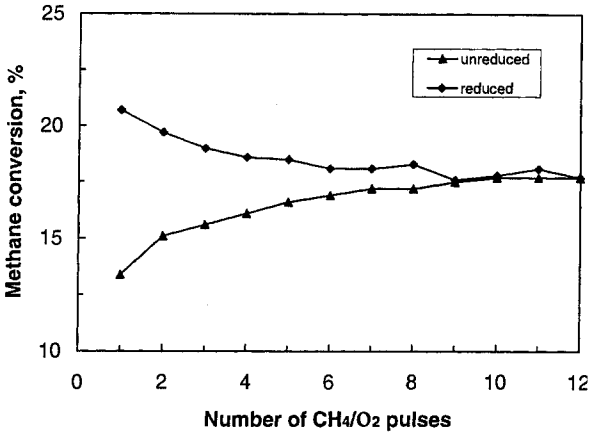

Fig. 2. CH_4 conversion as a function of number of CH_4/O_2 pulses.

function of the number of CH_4/O_2 pulses over the freshly prepared Ni/La_2O_3 catalyst (which contains nickel oxide), and over the catalyst reduced in hydrogen. Over the fresh catalyst, the CH_4 conversion increased gradually with the number of pulses, reaching the constant value of about 18% after the 9th pulse. Over the reduced catalyst, the CH_4 conversion was the largest for the first pulse and reached after the 9th pulse the same constant value as for the fresh catalyst.

The change of the CO selectivity with the number of CH_4/O_2 pulses has features similar to those of the CH_4 conversion. For the freshly prepared catalyst, the CO selectivity increased and reached after the 9th pulse the constant value of 46% (fig. 3). For the reduced catalyst, the CO selectivity was the largest for the first pulse, decreased gradually afterwards, reaching after the 9th pulse the same constant value as for the freshly prepared catalyst.

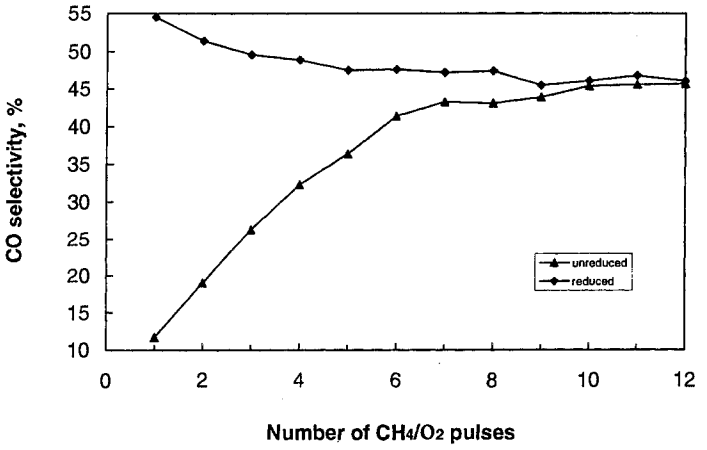

Fig. 3. CO selectivity as a function of number of CH_4/O_2 pulses.

3.2. EFFECT OF THE REACTANT RESIDENCE TIME ON SELECTIVITY

When the space velocity of the carrier gas was changed from 257143 to 400000 ($cm^3\ h^{-1}\ g^{-1}$), the CO selectivity increased gradually from 41 to 46% at 600°C, while that for CO_2 decreased (fig. 4). Of course, the larger the space velocity of the carrier gas , the shorter the residence time of reactants. Consequently, the generation of CO is favored by shorter residence times.

3.3. PULSES OF CH_4 OR O_2 OVER THE CATALYST PREVIOUSLY USED FOR CH_4/O_2 PULSES

After the catalyst was used 12 times for CH_4/O_2 (2/1) pulses, C_2H_4 and C_2H_6 as well as CO and CO_2 were detected (fig. 5) by MS for a CH_4 pulse. This implies that CH_4 dissociated, generating CH_x species ($CH_4 \rightarrow CH_x + (4-x)H$) and that some oxygen was still present on the catalyst. Over the catalyst used 12 times for CH_4/O_2 (2/1) pulses, CO and CO_2 were detected for an O_2 pulse (fig. 6). This suggests that some species containing carbon were still present on the catalyst.

4. Discussion

4.1. ACTIVE SITE OF THE Ni/La_2O_3 CATALYST

The effect of the catalyst state on CH_4 activation is clearly demonstrated by figs. 2 and 3. As the number of CH_4/O_2 pulses increased, the CH_4 conversion and CO selectivity increased over the fresh Ni/La_2O_3 and decreased over the reduced catalyst. However, for both kinds of catalysts, the CO selectivity and CH_4 conversion evolved towards the same constant values as the number of CH_4/O_2 pulses

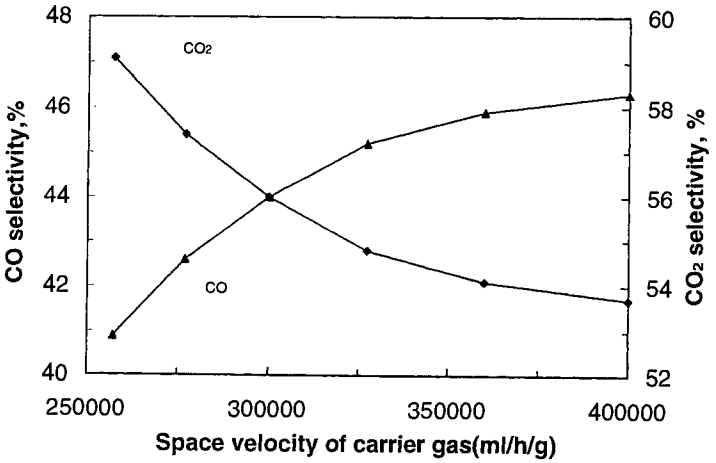

Fig. 4. CO/CO_2 selectivities as a function of space velocity of the carrier gas.

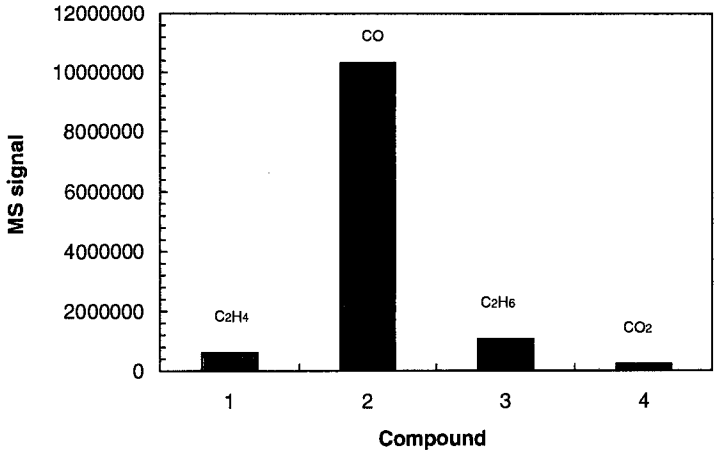

Fig. 5. The mass spectrum of CH_4 pulse over the catalyst previously used 12 times for CH_4/O_2 pulses.

increased. This indicates that the oxide state and reduced state of the catalyst changed towards the same state as the number of CH_4/O_2 pulses increased. In other words, the oxide state of the catalyst was partially reduced, whereas the reduced catalyst was partially oxidized, and finally the redox equilibrium of the catalyst was attained. Lunsford and coworkers observed that both the reduced and the oxidized Ni were present in the Ni/Al_2O_3 catalyst used in the CH_4 oxidation [6]. This is consistent with our results. One can see from fig. 2 that as the catalyst is reduced, the CH_4 conversion increases. This implies that the reduced Ni is more favorable to CH_4 activation than the Ni oxide. Campbell et al. reported that the reaction probability of methane on NiO films is significantly lower than that over clean Ni(100) surfaces [22]. Therefore, one can conclude that the reduced Ni state constitutes the main active site.

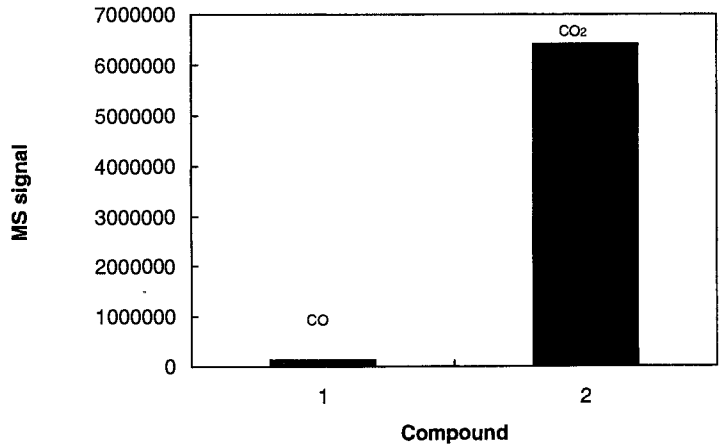

Fig. 6. The mass spectrum of O_2 pulse over the catalyst previously used 12 times for CH_4/O_2 pulses.

4.2. REACTION MECHANISM OF CH_4 OXIDATION

When the catalyst used in CH_4/O_2 reaction was exposed to a CH_4 pulse, the mass spectrum showed that CO, CO_2, C_2H_4 and C_2H_6 were generated (fig. 5). The presence of C_2H_4 and C_2H_6 indicates that the catalyst dissociates CH_4 to CH_x species. The fact that the amount of CO generated was much larger than those of C_2H_4 and C_2H_6 implies that CH_x oxidation is a faster pathway than its coupling. In the mass spectrum of the O_2 pulse over the catalyst used in the CH_4/O_2 pulse reaction, CO and CO_2 were detected. This means that species containing carbon are present on the catalyst for the CH_4/O_2 pulse. Therefore, it is reasonable to conclude that CH_4 dissociates to CH_x during the CH_4 oxidation reaction.

As shown in fig. 3, the CO selectivity increased while that of CO_2 decreased as the space velocity was increased. This means that CO formation is favored by shorter residence times. Consequently, CO represents the direct product, whereas CO_2 is generated from CO. This is consistent with the pyrolysis mechanism in which CO is generated by the oxidation of C formed via the CH_4 dissociation [7–11]. Combining the above results, one can suggest that at low reaction temperatures (600°C), the CH_4 activation occurs mainly on the reduced sites of the catalyst and follows the mechanism:

$$\text{site} + CH_4 \rightarrow CH_{4(s)} \tag{4}$$

$$\text{site} + O_2 \rightarrow 2O_{(s)} \tag{5}$$

$$CH_{4(s)} \rightarrow CH_{3(s)} + H_{(s)} \tag{6}$$

$$CH_{3(s)} \rightarrow CH_{2(s)} + H_{(s)} \tag{7}$$

$$CH_{2(s)} \rightarrow CH_{(s)} + H_{(s)} \tag{8}$$

$$CH_{(s)} \rightarrow C_{(s)} + H_{(s)} \tag{9}$$

$$C_{(s)} + O_{(s)} \rightarrow CO_{(s)} \rightarrow CO_{(g)} \tag{10}$$

$$CO_{(s)} + O_{(s)} \rightarrow CO_{2(s)} \rightarrow CO_{2(g)} \tag{11}$$

$$H_{(s)} + H_{(s)} \rightarrow H_{2(s)} \tag{12}$$

$$H_{(s)} + O_{(s)} \rightarrow OH_{(s)} \tag{13}$$

$$OH_{(s)} + H_{(s)} \rightarrow H_2O_{(s)} \tag{14}$$

$$H_2O_{(s)} \rightarrow H_2O_{(g)} \tag{15}$$

Table 1
Activation energies for dissociation of CH_4

Reaction step	Activation energy (kcal/mol)	
	Ni(111)	Ni(100)
$CH_{4(s)} \rightarrow CH_{3(s)} + H_{(s)}$	15	14
$CH_{3(s)} \rightarrow CH_{2(s)} + H_{(s)}$	22	24
$CH_{2(s)} \rightarrow CH_{(s)} + H_{(s)}$	23	23
$CH_{(s)} \rightarrow C_{(s)} + H_{(s)}$	5	5

4.3. EFFECT OF THE ADSORBED OXYGEN ON CH_4 DISSOCIATION

The above mechanism implies that CH_4 dissociation is a most important step. However, it is not yet clear whether the adsorbed oxygen promotes the CH_4 dissociation. In order to clarify this point, we compared the CH_4 dehydrogenation, with and without involvement of oxygen, calculating the activation energies on the Ni (100) and (111) surfaces with the bond-order conservation Morse-potential (BOC-MP) approach [19–21]. Three types of oxygen species were considered: those on-top, bridge and hollow sites. The results are listed in tables 1 and 2, which show that only the oxygens located at on-top sites decrease the activation energy for the dehydrogenation of methane; the oxygens located on bridge or hollow sites increase the activation energy. The oxygens at on-top sites are in a weak bonding state. Consequently, they either participate to a chemical reaction or move to more stable sites (hollow sites). One can conclude that only the transient oxygen species weakly adsorbed on metals promote the dehydrogenation of CH_4.

5. Conclusion

(i) The reduced Ni state constitutes the main active site; (ii) CO is the direct product and the CH_4 oxidation conversion follows the pyrolysis mechanism (at least at the low temperature of 600°C); (iii) the transient oxygen species adsorbed weakly on metal (on-top sites) can promote the dehydrogenation of CH_4.

Table 2
Activation energies for dissociation of CH_4

Reaction step	Activation energy (kcal/mol)					
	Ni(111)			Ni(100)		
	on-top	bridge	hollow	on-top	bridge	hollow
$CH_4 + O_{(s)} \rightarrow CH_{3(s)} + OH_{(s)}$	5	24	33	0	15	21
$CH_3O_{(s)} \rightarrow CH_{2(s)} + OH_{(s)}$	11	30	39	8	25	31
$CH_2O_{(s)} \rightarrow CH_{(s)} + OH_{(s)}$	12	31	40	7	25	30
$CH + O_{(s)} \rightarrow C_{(s)} + OH_{(s)}$	0	20	32	0	11	18

Appendix: BOC-MP approach

The basic parameter of this approach is the maximum metal–adsorbate (M–A) two-center bond energy (Q_{0A}), which can be obtained from the experimental heat of atomic chemisorption (Q_A), via the expression [19]

$$Q_A = Q_{0A}(2 - 1/n), \tag{A1}$$

where n is the coordination number of the chemisorbed atom A. The molecular chemisorption heat (Q_{AB}) for the case in which only A is coordinated to the metal atoms can be calculated using the following equations:

(i) weak M_n–AB bonding

$$Q_{AB} = Q_{0A}^2/[(Q_{0A}/n) + D_{AB}], \tag{A2}$$

(ii) strong Mn–AB bonding

$$Q_{AB} = Q_A^2/(Q_A + D_{AB}), \tag{A3}$$

(iii) intermediate M_n–AB bonding

$$Q_{AB} = \tfrac{1}{2}\{Q_{0A}^2/[(Q_{0A}/n) + D_{AB}] + Q_A^2/(Q_A + D_{AB})\}, \tag{A4}$$

where Q_A is the chemisorption heat of the coordinated atom A, and D_{AB} is the heat of dissociation of A–B in the gas phase.

The activation energy can be calculated using the following equations:

(i) for the $AB_{(s)} \rightarrow A_{(s)} + B_{(s)}$ reaction

$$\Delta E = \tfrac{1}{2}\{D_{AB} + [Q_A Q_B/(Q_A + Q_B)] + Q_{AB} - Q_A - Q_B\}, \tag{A5}$$

(ii) for the $A_{(s)} + BC_{(s)} \rightarrow [A\cdots B\cdots C] \rightarrow AB_{(s)} + C_{(s)}$ reaction

$$\Delta E = \tfrac{1}{2}\{D + [Q_{AB}Q_C/(Q_{AB} + Q_C)] + Q_A + Q_{BC} - Q_{AB} + Q_C\}, \tag{A6}$$

where $D = D_A + D_{BC} - D_{AB} - D_C$.

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