Near 100% CO selectivity in CH_4 direct catalytic oxidation at low temperatures (< 700°C) under unsteady state conditions

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Almost 100% CO selectivity was achieved with small pulses of CH_4/O_2 (2/1), using very short residence times over a reduced NiO/La_2O_3 catalyst. One concludes that CH_4 conversion depends on its dissociation, whereas CO selectivity is mainly dependent on the strength of oxygen binding to the catalyst. Over the reduced catalyst, the oxygen species oxidize with difficulty (because of their strong binding to metal Ni) CO to CO_2, whereas over the unreduced catalyst (which contains Ni oxide), the oxygen species easily oxidize (because they are weakly adsorbed) CO to CO_2.

Keywords: CH_4; syngas; nickel; unsteady state

The conversion of CH_4 to useful products has a major importance in chemical industry. Although the oxidative coupling of CH_4 to ethane and ethylene is a topic of active research, it still has limited significance because of the low conversion of CH_4 and low selectivity [1,2]. A more efficient route to useful products is via the syngas intermediate (CO and H_2 mixture), which can easily generate either methanol over Cu/Zn/Al catalysts or hydrocarbons over Fe catalysts [3,4]. Recently, it was reported that CO and H_2 can be produced from CH_4 by direct partial oxidation in steady state over some transition metal catalysts [5–11]. Ashcroft et al. [5] noted that, for a CH_4/O_2 ratio of 2/1, CO formation is favored to CO_2 formation for $T > 693°C$. Choudhary et al. [10,11] observed that at high space velocities and temperatures greater than 700°C, the methane conversion and CO selectivity were close to the equilibrium values, whereas, below 700°C, the CO selectivity exceeded the prediction of thermodynamic equilibrium [10,11]. Lunsford et al. [7], investigating the steady state direct partial oxidation of methane over Ni/Yb_2O_3 catalyst, found

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that hot spots were present in the catalyst bed, and concluded that the hot spots, which can have temperatures that are 300°C higher, were responsible for the observation of Choudhary's group below 700°C. They [7] also noted that below 700°C the CO selectivity is controlled by thermodynamic equilibrium. In the present work, we report that near 100% CO selectivity can be achieved over 20 wt% Ni/La_2O_3 catalysts under unsteady state conditions, using small pulses of CH_4/O_2 (2/1), high flow rates of the carrier gas and low temperatures (450–700°C). Since the pulses are very small, hot spots are unlikely to occur. We verified this experimentally, using a split furnace and visually observing whether a hot spot was formed as the reagents passed over the catalyst.

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 generated paste 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. A quartz tube (2 mm diameter) was used as reactor. The catalyst powder (weight: 0.02 g, bed height: 2 mm) was held on quartz wool. The catalyst was reduced with H_2 (20 ml/min) at 600°C for 2 h. The reactants, CH_4/O_2 (2/1), contained 10% argon as an inert internal standard, and pulses of 45 μl were employed. Ultra high purity helium at a high flow rate (300000 $cm^3\ g^{-1}\ h^{-1}$) was used as gas carrier. The analysis of gases during 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.

The data in table 1 show that CO selectivity was nearly 100% for CH_4/O_2 pulses, at low temperatures (450–700°C), over the freshly reduced NiO/La_2O_3 catalyst. Since the thermodynamic equilibrium indicates that below 700°C the formation of CO_2 is favored (table 2), it is clear that the process is controlled by kinetics. The unreduced catalyst, which contains Ni oxide, had a much lower CH_4 conversion and CO selectivity than the freshly reduced catalyst.

Table 1
Results for the catalytic reaction of CH_4/O_2 (2/1) at low temperatures ($\leqslant$700°C)

Temperature (°C)	CH_4 conversion (%)	CO selectivity (%)
reduced catalyst		
700	95	100[a]
600	87	100[a]
500	30	99
450	8	100[a]
unreduced catalyst		
700	23	7
600	8	1
500	<0.1	8
450	<0.1	63

[a] Containing micro amount of CO_2.

Table 2
Thermodynamic equilibrium data for methane oxidation [8] [a]

Temperature (°C)	CH_4 conversion (%)	CO selectivity (%)
300	26	0.2
400	29	3
500	38	20
600	55	59
700	78	88
800	92	97
900	97	99

[a] Initial $CH_4 : O_2 = 2 : 1$, at total pressure of 1 atm.

Fig. 1 shows dynamic responses of CH_4 and CO for a CH_4/O_2 (2/1) pulse, and the dynamic response of CO for a CO pulse, over the reduced NiO/La_2O_3 catalyst. One can see that the CO response curve in the CH_4/O_2 pulse had a much longer time for the peak and a much longer tail than the CH_4 response curve in the same pulse and the CO response curve for the pure CO pulse. This indicates that the CH_4 adsorption and desorption and the CO desorption are fast compared to CO generation. One can therefore conclude that CH_4 dissociates fast to C species and that the reaction between the C species and surface oxygen, which leads to CO, is rate-determining (RDS). In other words, the reaction mechanism over the reduced catalyst can be written in the form:

$$CH_{4(g)} \rightarrow \ldots \rightarrow C_{(s)} + 4H_{(s)} \qquad (1)$$

$$O_{2(g)} \rightarrow 2O_{(s)} \qquad (2)$$

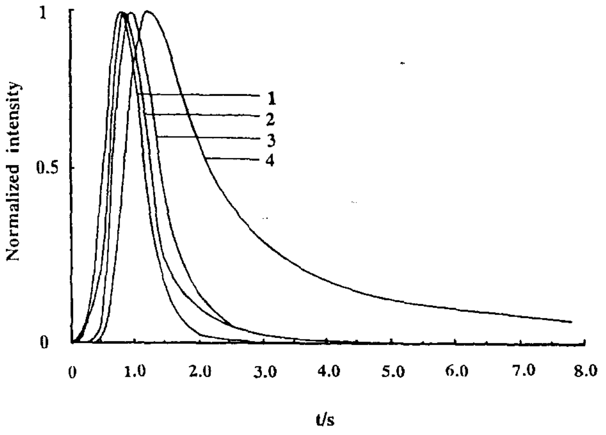

Fig. 1. Dynamic response curves of Ar (1), CH_4 (2), CO (4) for a CH_4/O_2 (2/1) pulse and the dynamic response curve of CO (3) for a CO pulse at 600°C.

$$C_{(s)} + O_{(s)} \rightarrow CO_{(s)} \quad \text{(RDS)} \tag{3}$$

$$CO_{(s)} \rightarrow CO_{(g)} \tag{4}$$

$$CO_{(s)} + O_{(s)} \rightarrow CO_{2(s)} \rightarrow CO_{2(g)} \tag{5}$$

$$H_{(s)} + H_{(s)} \rightarrow H_{2(s)} \rightarrow H_{2(g)} \tag{6}$$

Over the unreduced catalyst and at relatively low temperatures (⩽500°C), the reaction mechanism is probably similar to that over the reduced catalyst, with the difference that the NiO site is less active than the Ni site. At high temperatures (700°C), the mechanism becomes more complicated because CH_4 reduces some of the NiO to Ni and the activity over the latter site is as high as over the reduced catalyst. However, for very small pulses and very short residence times, it is likely that the number of reduced sites will be small.

The results of table 1 can be explained as follows. CH_4 dissociates much easier over the reduced catalyst than over the unreduced catalyst (containing Ni oxide) [12]. For this reason, the activity is much higher over the former than over the latter. Because the oxygen species are strongly adsorbed on the metal Ni [13], they oxidize with some difficulty the CO molecules to CO_2. Over the unreduced catalyst, the oxygen species have a weak binding to Ni oxide [14]. For this reason, they can easily oxidize CO to CO_2, even before CO molecules desorb. When the temperature was decreased to 450°C, the lower temperature decreased the rate of reaction between CO and oxygen species. As a result, the unreduced catalyst had a higher CO selectivity at 450°C than at the higher temperatures (⩾500°C).

In the present work, small pulses (45 µl) $CH_4/O_2/Ar$ and very short residence times (3.8 ms) were employed, in order to minimize the oxidation of the reduced catalyst during the pulse reaction. When, however, 900 µl pulses of CH_4/O_2 were employed over a reduced catalyst, we found that at 600°C the CH_4 conversion and CO selectivity decreased to 21 and 55%, respectively. This shows that the oxygen of the pulse oxidizes partially the catalyst and the oxygen weakly adsorbed on the oxidized surface decreases the CO selectivity. Consequently, both CH_4 conversion and CO selectivity increase with the extent of reduction of the catalyst. This explains the change in the same direction [9–11] of the CH_4 conversion and CO selectivity.

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