Catalysis Letters Vol. 85, Nos. 1–2, January 2003 (© 2003)

NO_x-catalyzed gas-phase activation of methane: a reaction study

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Received 17 July 2002; accepted 3 October 2002

The catalytic effect of NO_x on methane oxidation in the absence of any solid catalyst has been investigated. The experimental results show that NO_x has very good catalytic activity in the partial oxidation of methane. The predominant products for reactions in a CH_4–O_2–NO_x co-feed mode are CO, CO_2, H_2O and H_2, CH_3OH, HCHO, and C_2H_4. Aromatics are also observed.

KEY WORDS: gas-phase oxidation; methane activation; NO_x; syngas; ethylene.

1. Introduction

Catalytic activation of methane via pure gas-phase reactions in the absence of any solid catalyst, to produce different products such as oxygenates, syngas ($CO + H_2$), or aromatics by varying the reaction conditions, has not received sufficient attention. Over 70 years ago, Layng and Soukup noticed that small amounts of NO_2 can promote the oxidation of methane and ethane [1]. The main product was CO. Since then, however, little progress has been made. Otsuka and others [2–8] have recently reported that gas-phase oxidation of methane using NO as a catalyst can produce significant amounts of oxygenates ($HCHO + CH_3OH$). However, the formation of C_2H_4 and aromatics has not been reported. It is also worth noting that in order to promote the decomposition of hydrocarbons (benzene, xylenes), catalytic amounts of ferrocene have been vaporized and carried into the reaction tube where carbon nanotubes are prepared [9–11]. This indicates that gas-phase activation of hydrocarbons in which a solid catalyst is not present may have broad implications for research in different areas.

Methane, as the most important hydrocarbon source, has been the subject of many studies. In these different research areas, for example, partial oxidation of methane (POM), selective catalytic reduction (SCR) of NO_x, selective oxidation of methane (SOM) to oxygenates, and catalytic combustion of methane, the main reaction involves a three-component CH_4–O_2–NO_x system, and a solid catalyst. The possibility of some additional activation of methane by a purely gas-phase side reaction has been widely mentioned. For example, the importance of gas-phase reactions in the overall SCR mechanism has been recently briefly discussed [12]. The promotional effects of NO on SOM over a V_2O_5/SiO_2 catalyst [13], and on POM over various oxide catalysts [14] have been observed. Although Otsuka *et al.* proposed a very general relationship between the OCM (oxidative coupling of methane) and SCR activities of lanthanide oxides [15], the formation of C_2H_4 via a gas-phase reaction has not been clearly demonstrated.

In this paper, the catalytic effect of NO_x on methane oxidation in the absence of any solid catalyst has been investigated. The production of CO, HCHO, CH_3OH, and C_2H_4 was measured by on-line gas chromatography (GC) and FTIR spectroscopy under different reaction conditions [16].

2. Experimental

The experiments were carried out at atmospheric pressure in a conventional gas flow system with an empty quartz tube reactor (inner diameter 5 mm). The reactor was kept in a tubular furnace. The gases were controlled by mass flow controllers and premixed before entering the reactor. The temperatures indicated in this paper are the temperatures in the reaction zone of the reactor as measured with a thermocouple. The amounts of O_2, CH_4, H_2, and CO_2 in the products were analyzed by on-line gas chromatography. The amounts of NO, NO_2, CO, CH_4, HCHO, and C_2H_4 were determined by on-line FTIR spectroscopy using a Bruker Vector 22 spectrometer with a gas cell of 10 cm in length. The concentrations were determined automatically using the OPUS Quantitative Method with appropriate calibration curves. A condenser connected close to the outlet of the quartz tube (also the inlet into the on-line GC/IR) was used to collect possible liquid products.

3. Results and discussion

The products observed by on-line IR and GC, for reactions in a CH_4–O_2–NO_x co-feed ($CH_4/O_2 = 1$–5)

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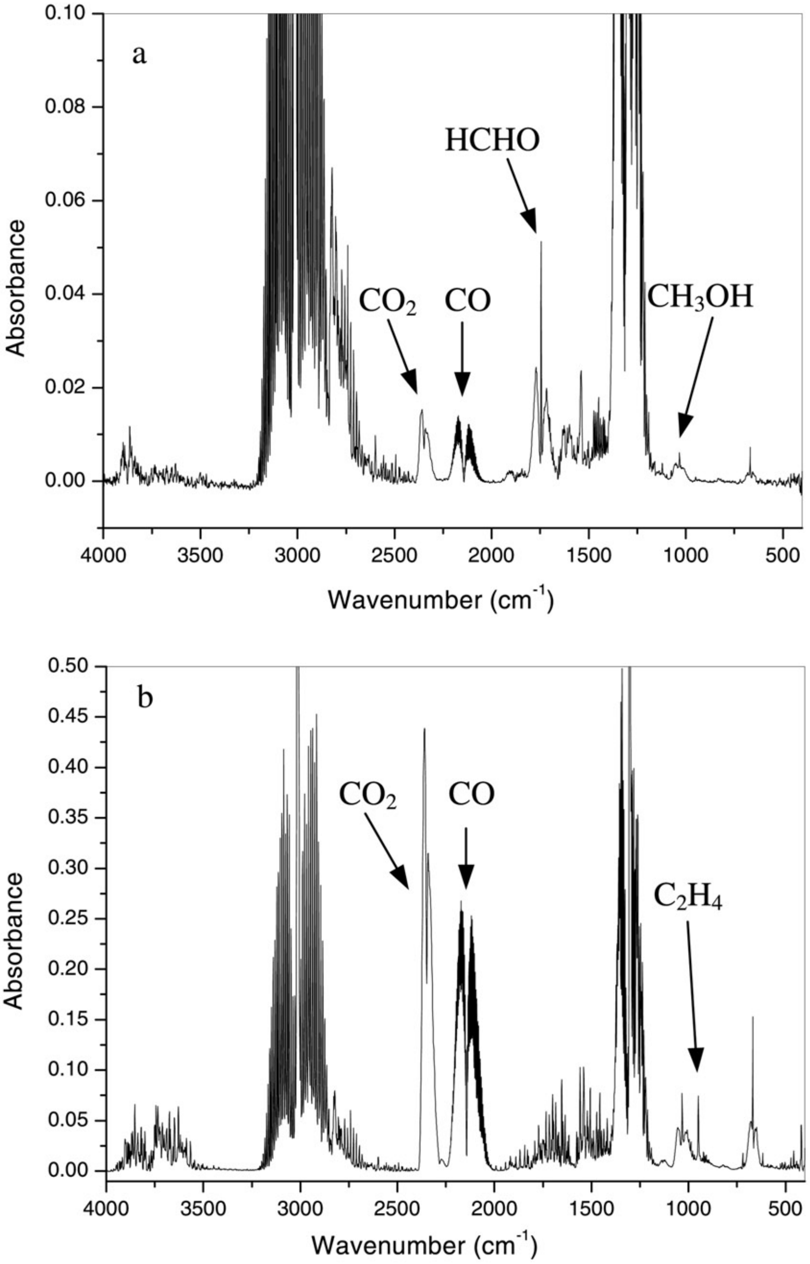

Figure 1. IR spectra of product mixtures. Reaction conditions: CH_4, 20%; O_2, 10%; NO, 600 ppm; N_2, balance; flow rate, 40 ml/min; temperature (a) 550 °C, (b) 700 °C.

mode, are CH_3OH, HCHO, C_2H_4, CO, CO_2, H_2O, and H_2. The percentages of CH_3OH, HCHO, and C_2H_4 are low, normally not greater than 1%. CO, CO_2, H_2O, and H_2 are the predominant products. IR spectra obtained at 550 and 700 °C with a CH_4/O_2 ratio of 2 are shown in figure 1. After running for several days, significant amounts of a white solid are observed at the outlet of the reactor. Based on IR analysis, this white solid is paraformaldehyde. Liquid products are also observed in the condenser. The results obtained from GC–MS analysis shown in table 1 confirm that the liquid products are toluene, phenol, and derivatives.

Figure 2 shows the effects of NO addition on the conversion of methane and oxygen, and on the yields of CO and H_2 at $CH_4/O_2 = 2$. Methane begins to react with oxygen at 750 °C in the absence of NO. When 600 ppm NO is added, the activation temperature decreases by about 200 °C and reaction is observed at 550 °C. At 700 °C the conversion of methane and the selectivity to CO are 32 and 72%, respectively. At temperatures higher than 750 °C, methane conversion continues to increase, while CO selectivity decreases, indicating that CO_2 is the major product. It is clear that the main reaction below 750 °C is methane oxidation

Table 1
Composition of the condensate

Name	Formula
Toluene	C_7H_8
Phenol, 3,5-(1,1-dimethylethyl)-	$C_{14}H_{22}O$
Diethyl phthalate	$C_{12}H_{14}O_4$
Naphthalene, 1,2,3-trimethyl-4-(*E*)-propenyl-	$C_{16}H_{18}$
Di-*n*-butyl phthalate	$C_{16}H_{22}O_4$
Di-*n*-octyl phthalate	$C_{24}H_{38}O_4$

Table 2
Effect of reaction conditions on the partial oxidation of methane

CH_4/O_2	Flow rate (ml/min)	CH_4 conversion (%)	CO yield (%)	H_2/CO
2 : 1	20	39.8	34.3	0.54
2 : 1	40	44.0	31.7	0.51
2 : 1	80	41.0	23.8	0.56
2 : 1	160	34.6	15.0	0.60
3 : 1	40	19.4	15.4	1.0
5 : 1	40	7.0	2.7	1.1

Reaction conditions: CH_4, 20%; NO, 600 ppm; temperature, 700 °C.

catalyzed by NO_x. Above 750 °C, direct reaction between methane and oxygen may occur. The maximum yields of CO are reached at 650–700 °C. Meanwhile, hydrogen is detected with H_2/CO ratios of 0.4–0.7. Table 2 lists methane conversions, CO yields, and H_2/CO ratios for a series of experiments.

Under strongly oxidizing conditions ($O_2/CH_4 = 5$), NO also exhibits considerable catalytic activity and selectivity (~68%) for the conversion of methane to CO. The results are summarized in figure 3 and table 3. It can be seen that, in the absence of NO, the temperatures required for the activation of CH_4 are higher than 800 °C. In the presence of NO, however, the activation temperature is reduced to below 570 °C. The lowest observed activation temperature for the activation of CH_4 is only 520 °C. The $T_{50\%}$ value (defined as the temperature at which there is 50% CH_4 conversion) is higher than 866 °C in the absence of NO, but is reduced to around 600 °C when NO is present.

Parallel experiments show that no reaction is observed for the CH_4–NO system (without free oxygen) under the reaction conditions, indicating that the formation of NO_2 is a prerequisite for the activation of CH_4. In all the experiments shown in table 1, no decrease of total $NO + NO_2$ concentrations (based on the area of the IR absorption peaks) is observed up to 950 °C, indicating that NO_2 and other possible nitrogen oxides cannot be reduced by CH_4 in the absence of a solid catalyst.

It can be seen that the reactivity in the partial oxidation of methane (without NO_x catalyst) depends significantly on the flow rate. When the flow rates increase from 20 to 40 to 80 ml/min, $T_{50\%}$ rises from 866 to 911 to 950 °C in steps of about 40 °C. The selectivity to CO improves slightly with increasing temperature. However, the influence of the flow rate on the NO-catalyzed reactions seems less significant. When the flow rate increases, $T_{50\%}$ increases in steps of about 20 °C and the selectivity to CO remains unchanged. Under strongly oxidizing conditions ($O_2/CH_4 = 5$), formation of C_2H_4 is only observed at the ppm level. No HCHO was detected. This indicates that the NO-catalyzed partial oxidation of methane is highly selective for production of CO (68%).

Figure 4 shows the influence of NO concentration in the feed on the partial oxidation of methane at 650 °C. Although the conversion of CH_4 and the yield of CO reach a maximum when the concentration of NO is 400–600 ppm, the highest TOF (turnover frequency, methane molecules converted per second per NO) of $40\,s^{-1}$ is obtained with an NO concentration of

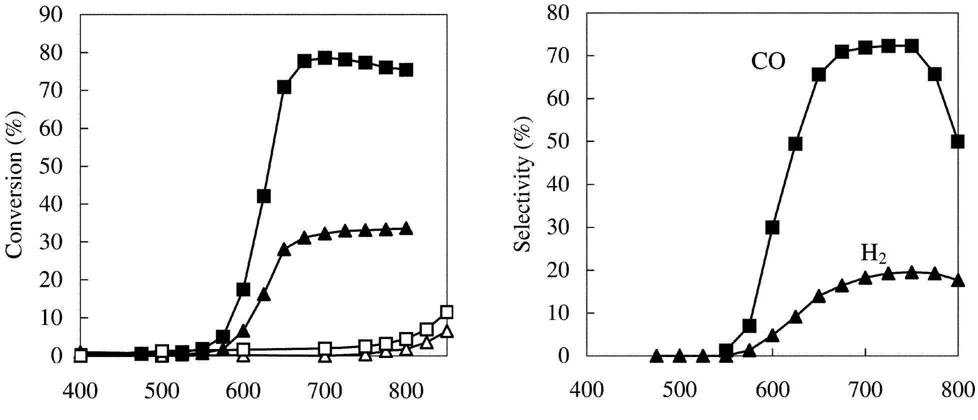

Figure 2. Effect of NO addition on conversion and selectivity at different temperatures: (a) CH_4 (△, ▲) and O_2 (□, ■) conversion in CH_4–O_2 (open symbols) and CH_4–O_2–NO (filled symbols) systems; (b) CO and H_2 selectivity. Reaction conditions: CH_4, 20%; O_2, 10%; NO, 600 ppm; N_2, balance; flow rate, 40 ml/min.

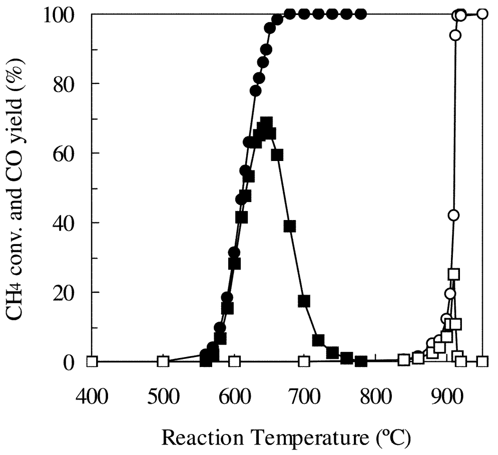

Figure 3. Effect of NO addition on CH_4 conversion (○, ●) and CO yield (□, ■). Open symbols refer to the NO-free system; filled symbols to the system containing 600 ppm NO. Reaction conditions: CH_4, 0.4%; O_2, 2%; NO, 600 ppm; flow rate, 40 ml/min.

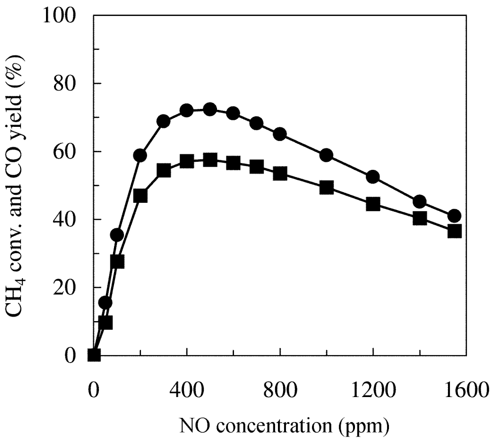

Figure 4. Effect of NO concentration on CH_4 conversion (●) and CO yield (■). Reaction conditions: CH_4, 0.4%; O_2, 2%; flow rate, 80 ml/min; temperature, 650 °C.

Table 3

CH_4 conversion and CO yield in the partial oxidation of methane[a]

NO (ppm)	Flow rate (ml/min)	Temperature range of CO formation (°C)	CO yield (maximum) (%)	CH_4 conversion at CO maximum (%)	Temperature of CO maximum (°C)	$T_{50\%}$ (°C)	TOF[c] (s^{-1})
–	20	800–880	16	79	868	866	–
–	40	840–920	25	42	910	911	–
–	80	875	30[b]	54[b]	>950	950	–
200	40	540–760	66	88	630	595	28
600	20	520–760	68	83	610	590	5
600	40	560–780	69	90	645	612	9
600	80	570–840	67	94	680	635	13

[a] Reaction conditions: CH_4, 0.4%; O_2, 2%; temperatures, 200–950 °C.

[b] Values measured at 950 °C.

[c] Values measured at 650 °C.

100 ppm. Similar results are also observed in the 20% CH_4–10% O_2 system, that is, CH_4 conversion and CO yield pass through a maximum with increasing NO concentration. The optimum NO concentration is 3000–5000 ppm. Since it is NO_2 and not NO that is the catalyst for the activation of methane, the temperature dependence of the equilibrium between NO and NO_2, i.e., $NO + \frac{1}{2}O_2 \leftrightarrow NO_2$, is responsible for the appearance of the maximum. Even so, the TOF is still higher than the average value obtained in conventional homogeneous catalysis in the liquid phase, suggesting that the reactions described here are gas-phase homogeneous catalytic reactions.

Furthermore, in comparison with the results of Fornasiero *et al.* [14], who observed a maximum CO selectivity of 59% at 730 °C over pure a ZrO_2 catalyst with CH_4 conversion of 85%, our results show that higher CO selectivity (>65%) can be observed at much lower temperature (by about 100 °C) in the absence of any solid catalyst. This shows that solids may not actually have any catalytic effect, and the importance of gas-phase reactions should be considered in future research on similar systems containing CH_4, O_2, and NO_x.

Acknowledgment

This project was supported by the Ministry of Science and Technology, China (G1999022202).

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