Homogeneous Partial Oxidation of Methane Catalyzed by NO_x under Oxidizing Conditions*

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Abstract The promotional effects of NO_x on the gas-phase oxidation of methane have been studied in the absence of solid catalysts. NO_x showed an obvious catalytic activity for the partial oxidation of methane to carbon monoxide, even under strong oxidizing conditions ($\text{O}_2/\text{CH}_4 = 5$). The addition of 0.005% ~ 0.2% NO in the $\text{CH}_4\text{-O}_2$ system decreased the reaction temperatures by 200 ~ 300 °C. Formaldehyde and ethylene were also observed in the products, and their relative concentrations were partially controlled by reaction conditions.

Keywords: Methane oxidation, Catalytic effect of NO_x , Homogeneous catalysis, Catalytic combustion

Catalytic conversion and catalytic combustion of methane have received extensive attention because of their potential to synthesize useful chemicals and to reduce pollutant emissions. Both processes require activation of methane, which has been mostly achieved over solid catalysts to date.

As early as 1928, Soukup *et al.*^[11] reported the partial oxidation of methane and ethane promoted by small amounts of NO_2 . However, only in the recent several years, the promotional effects of NO_x on the oxidation of methane or other alkanes have received more attention^[2-8]. Bañares *et al.*^[5] reported a favorable effect of NO for the selective oxidation of methane to CH_3OH and HCHO over $\text{V}_2\text{O}_5/\text{SiO}_2$ catalysts. Otsuka *et al.*^[6, 7] obtained > 6% yield for oxygenates ($\text{HCHO} + \text{CH}_3\text{OH}$) in the gas phase oxidation of methane catalyzed by NO. It is noteworthy that all these reactions were carried out with an excess of methane ($\text{O}_2/\text{CH}_4 = 0.1 \sim 0.5$). Recently, Kašpar *et al.*^[8] reported that the catalytic combustion of methane over ZrO_2 -, Al_2O_3 -, CeO_2 -based oxide catalysts could

be promoted by the addition of catalytic amounts of nitric oxide to the feed under strong oxidizing conditions, leading to a remarkable increase in CO formation. This paper shows that under either weak or strong oxidizing conditions ($\text{O}_2/\text{CH}_4 = 1.5 \sim 5$), NO_x can act as a good catalyst for the partial oxidation of methane to CO without the use of any solid catalyst.

The experiments were carried out in a conventional gas flow system with an empty quartz tube reactor (inner diameter 5 mm). 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 thermal couple. O_2 , CH_4 and CO_2 in the products were analyzed by on-line gas chromatography. NO, NO_2 , CO, CH_4 , HCHO , and C_2H_4 were analyzed by on-line FT-IR using a Bruker Vector 22 spectrometer with a gas cell of 10 cm length. The concentrations were determined automatically using OPUS quantitative method with appropriate calibration curves.

Fig. 1 Effect of NO addition (open symbols) on CH₄ conversion (○ ●) and CO selectivity (□ ■)

CH₄ 1.7%, O₂ 2.6%, NO 0.06%, flow rate 40 mL · min⁻¹

Fig. 1 shows the effect of NO addition on the conversion of CH₄ and the selectivity to CO under weak oxidizing conditions (O₂/CH₄ = 1.5). In the absence of NO, the oxidation of CH₄ requires temperatures higher than 850 °C. In the presence of NO, the reaction starts at a lower temperature, ca. 550 °C, and the selectivity to CO is about 40% at a temperature of 650 °C.

At the same time, formaldehyde and ethylene are observed in the products. Fig. 2 shows the infrared spectra of the feed gas and the product mixture after the reaction. The spectrum of the product mixture shows the

Fig. 2 Gas-phase FT-IR spectra of (a) feed gas and (b) product gas after reaction at 600 °C reaction condition as reported in Fig. 1

infrared absorption bands of CO (2 200 ~ 2 100 cm⁻¹), NO (1 930 ~ 1 830 cm⁻¹), HCHO (1 745 cm⁻¹), NO₂ (1 628, 1 600 cm⁻¹) and C₂H₄ (949 cm⁻¹, not shown in the figure). The optimum temperature for the formation of HCHO is in the range of 600 ~ 800 °C, whilst that for the formation of C₂H₄ is 650 ~ 900 °C.

Under strong oxidizing conditions (O₂/CH₄ = 5), NO also exhibits considerable catalytic activities and selectivity (~68%) for the conversion of methane to CO. The results are summarized in Table 1 and Fig. 3. It can be seen that, in the absence of NO, the temperatures required for the activation of CH₄ are

Table 1 CH₄ conversion and CO selectivity in the partial oxidation of methane^a

NO (%)	v mL · min ⁻¹	Temperature range of CO formation (°C)	CO selectivity (maximum) ^b (%)	CH ₄ conversion at CO maximum (%)	Temperature of CO maximum (°C)	$T_{50\%}$ °C	TOF ^d (s ⁻¹)
/	20	800 ~ 880	16	79	868	866	/
/	40	840 ~ 920	25	42	910	911	/
/	80	875	30 ^c	54 ^c	> 950	950	/
0.02	40	540 ~ 760	66	88	630	595	28
0.06	20	520 ~ 760	68	83	610	590	5
0.06	40	560 ~ 780	69	90	645	612	9
0.06	80	570 ~ 840	67	94	680	635	13

^aReaction conditions: $x(\text{CH}_4) = 0.4\%$; $x(\text{O}_2) = 2\%$; temperature: 200 ~ 950 °C

^bCO selectivity: $n_{\text{CO}} \cdot (n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{CH}_4}) / \text{mol}$

^cValues measured at 950 °C

^dValues measured at 650 °C

Fig. 3 Effect of NO addition (open symbols) on CH₄ conversion (○ ●) and CO selectivity (□ ■)
CH₄ 0.4%, O₂ 2%, NO 0.06%, flow rate 40 mL · min⁻¹

higher than 800 °C. However, in the presence of NO, the activation temperature is reduced to below 570 °C. The lowest temperature for the activation of CH₄ is only 520 °C. The $T_{50\%}$ (defined as temperature for 50% CH₄ conversion) is higher than 866 °C in the absence of NO, but this is reduced to around 600 °C when NO is present. Parallel experiments show that no reaction is observed for CH₄-NO (without free-oxygen) system under the reaction conditions, indicating that the formation of NO₂ is a prerequisite for the activation of CH₄. In all the experiments whose results are shown in Table 1, no decrease of NO/NO₂ concentrations (based on the area of infrared absorption) is observed up to 950 °C, indicating that NO₂ and other possible nitrogen oxides cannot be reduced by CH₄ in the absence of a solid catalyst. It can be seen from Table 1 that the reactivity of the partial oxidation of methane (without NO_x catalyst) depends significantly on the flow rate (v). When the flow rate increases from 20 to 40 to 80 mL · min⁻¹, the $T_{50\%}$ rises from 866 to 911 to 950 °C in a step 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, the $T_{50\%}$ increases in steps of about 20 °C and the selectivity to CO remains unchanged. Under strong oxidizing conditions (O₂/CH₄ = 5), formation of C₂H₄ is only observed at 10⁻⁶ level. No HCHO was detect-

Fig. 4 Effect of NO concentration on CH₄ conversion (●) and CO selectivity (■)

CH₄ 0.4%, O₂ 2%, flow rate 80 mL · min⁻¹, temperature 650 °C

ed. This indicates that the NO-catalyzed partial oxidation of methane is highly selective for production of CO (68%).

Fig. 4 shows the influence of NO concentration in the feed on the partial oxidation of methane at 650 °C. Although the conversion of CH₄ and the selectivity to CO reaches a maximum when NO is 0.04% ~ 0.06%, the highest TOF (turnover frequency, methane molecules converted per second per NO) of 40 is obtained with an NO concentration of 0.01%. The formation of NO₂ clearly implies that either NO or NO₂ is actually the catalyst precursor rather than the actual catalyst. Even so, the TOF is still higher than the average value obtained in conventional homogeneous catalysis in liquid-phase, suggesting that the reactions described here are gas-phase homogeneous catalytic reactions.

Furthermore, in comparison with the results of Kašpar *et al.*, who observed a maximum CO selectivity of 59% at 730 °C over pure ZrO₂ catalyst with CH₄ 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. The selectivity to oxygenates or to CO may change with the conditions. Because the catalytic efficiency is very high and the system is simple, it provides an excellent opportunity for *in situ* investigation of the mechanism and the factors controlling the activ-

ity and selectivity in catalytic partial oxidation of methane. In addition, the catalytic activity of NO_x demonstrated in this work may have practical application in the catalytic conversion and catalytic combustion of methane in view of the advantages of gas-phase reactions over heterogeneous reactions.

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氧化条件下 NO_x 催化的甲烷均相部分氧化 *

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摘要 考察了没有固体催化剂时 NO_x 对甲烷气相氧化的促进作用. 实验结果表明, 即使在强氧化条件下 (O₂/CH₄ = 5), NO_x 对甲烷部分氧化制一氧化碳仍然有明显的催化活性. 在 CH₄-O₂ 体系中加入 0.005% ~ 0.2% 的 NO 后, 反应温度可降低 200-300 °C. 在反应产物中还可观察到甲醛和乙烯, 通过改变反应条件可以控制它们的相对浓度.

关键词: 甲烷氧化, NO_x 催化, 均相催化, 催化燃烧

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