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Partial oxidation of light alkanes by NO_x in the gas phase

K. Otsuka*, R. Takahashi, K. Amakawa, I. Yamanaka

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Abstract

Partial oxidations of CH_4, C_2H_6, C_3H_8, and iso-C_4H_{10} with O_2 were promoted by addition of NO in the gas phase. The addition of NO increased the conversion rate of alkanes and decreased the initiation temperatures for the reactions. Moreover, selectivities and yields to oxygenates, aldehydes, ketones and alcohols, were remarkably improved by the addition of NO. The maxima of one-pass yields of oxygenates were 7% for CH_4, 11% for C_2H_6, 13% for C_3H_8, and 29% for iso-C_4H_{10}. It is suggested that NO_2 produced from NO and O_2 is the initiator for the oxidation of light alkanes. Alkyl nitrite was proposed as the reaction intermediate for the formation of oxygenates. The alkyl nitrite decomposes into oxygenates and NO that works as catalyst for the activation of O_2 and the oxidation of alkanes.

Keywords: Partial oxidation; CH_4; C_2H_6; C_3H_8; NO_x

1. Introduction

De-NO_x is one of the most important subjects for sustaining the lives of creature on the earth because NO_x are poisons due to their high reactivities against organic compounds. However, we believe that this high reactivity of NO_x could be applied for activation and oxidation of alkanes, synthesizing useful oxygenates.

Chemical utilization of natural gas (CH_4, C_2H_6, and C_3H_8) as a feed stock is an attractive subject for chemical industry. However, it is difficult to convert light alkanes directly into useful oxygenates, such as aldehydes, ketones, and alcohols, due to their low reactivities. Many chemists have studied a great number of catalytic oxidation systems [1–3] and non-catalytic radical chain reactions in the gas phase [4] to convert light alkanes, especially CH_4, to oxygenates. However, one-pass yields for the sum of HCHO and MeOH were lower than 5% for most of the works reported so far for the oxidation of CH_4. Irusta [5] and Haruta [6] recently reported the effect of NO (HNO_3) on the oxygenation of CH_4 to HCHO (<4% yield) in the gas phase at 560°C. Since long time ago, it has been known that the oxidation of CH_4 with O_2 can be accelerated by addition of NO [7]. However, detailed reaction mechanism for the formation of HCHO has not been cleared yet. Moreover, there are a few studies focusing on the formation of oxygenates from C_2H_6 and C_3H_8 catalyzed by NO in the gas phase.

The aims of this work are to demonstrated the effect of NO on the formation of oxygenates especially from C_2H_6, C_3H_8, and iso-C_4H_{10} and to get informations about the reaction mechanism of the formation of the oxygenates.

2. Experimental

The oxidations of light alkanes, CH_4, C_2H_6, C_3H_8 and iso-C_4H_{10}, were carried out by using a conven-

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*Corresponding author. Tel.: +81-3-5734-2143; fax: +81-3-5734-2879; e-mail: kotsuka@o.cc.titech.ac.jp

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tional gas flow system. Standard experimental procedure was as follows. A gas mixture of light alkanes (20 kPa), O_2 (10 kPa), NO (2 kPa), balanced with He (total pressure 101 kPa, total flow rate $=120\ \mathrm{ml\ min^{-1}}$) was introduced to a quartz tube reactor (i.d. 8 mm) at 450–650°C. Products were analyzed by an on-line gas chromatograph (Shimazu GC8A TCD with Porapak-Q, Porapak-T, and Molecular Sieve 5A columns). Conversions of alkanes, selectivities to products and product yields were calculated on the basis of the carbon numbers of the reactant alkanes.

3. Results and discussion

Fig. 1 shows the effects of addition of NO on the conversion rates of CH_4, C_2H_6, and C_3H_8. In the absence of NO, the oxidations of C_3H_8 and C_2H_6 required the temperature above 500°C and that of CH_4 did not occur at <650°C under this experimental conditions.

When NO was added to a mixture of alkane and O_2, the oxidations of C_3H_8 and C_2H_6 proceeded at 400°C, i.e., 100°C lower temperature than those in the absence of NO. Moreover, oxidation of CH_4 initiated at >450°C by addition of NO. When a mixture of C_3H_8, C_2H_6, or CH_4 with NO was introduced to the reactor without O_2, no conversion of these alkanes took place at 600°C. These results indicate that NO promotes the oxidations of light alkanes only in the presence of O_2. The turnover numbers for the conversions of alkanes based on the NO introduced were 2.3 for C_3H_8 (500°C), 2.8 for C_2H_6 (550°C), and 2.9 for CH_4 (650°C). These results suggest that NO works as a catalyst for the oxidation of the light alkanes.

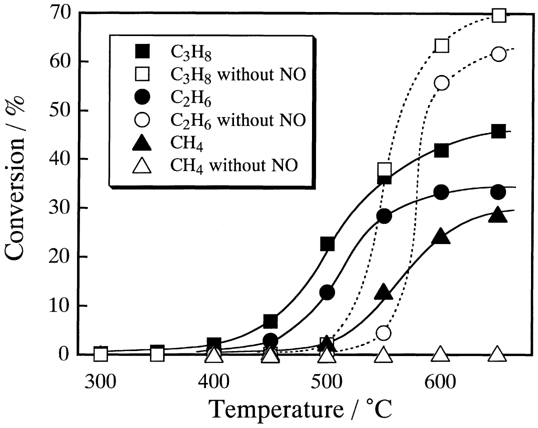

Fig. 1. Effect of the addition of NO on the conversion for the oxidations of light alkanes.

Table 1
Activation energy for the conversion rates of light alkanes with O_2 in the gas phase

	Activation energy ($\mathrm{kJ\ mol^{-1}}$)		
	C_3H_8	C_2H_6	CH_4
Without NO	275	361	—
With NO	107	138	208

Apparent activation energies for the conversion of CH_4, C_2H_6, and C_3H_8 with O_2 or with NO and O_2 are summarized in Table 1. The values were calculated from the slopes of the ln r (r=conversion rate) vs. $1/T$ plots. The activation energies for the conversion of C_2H_6 and C_3H_8 dramatically decreased by the addition of NO, as can be seen in Table 1. The activation energy for the oxidation of CH_4 with O_2 was not obtained because the oxidation of CH_4 did not proceed as described above. The activation energy for the oxidation of CH_4 with NO and O_2 was lower than those for the oxidations of C_2H_6 and C_3H_8 with O_2. These results suggest that the mechanisms for activation of the light alkanes with NO and O_2 are very different from the non-catalytic radical-chain oxidations of alkanes with O_2.

The selectivities of products for the oxidation of the light alkanes with NO and O_2 were also very different from those without NO. Fig. 2 shows the effects of temperature on the distribution of the products for the oxidation of C_3H_8 with O_2. Alkenes (C_3H_6 and C_2H_4) were the major products and the selectivities to oxygenates (MeCHO, HCHO, MeOH, EtOH, EtCHO, and Me_2CO) were less than 9% at the temperatures examined. While, in the presence of NO and O_2, much more oxygenates (MeCHO>HCHO>MeOH>EtOH, Me_2CO, EtCHO) were formed for the oxidation of C_3H_8 as indicated in Fig. 3. The selectivity to the sum of oxygenates is greater than 60% at <450°C. Nitroalkanes ($MeNO_2$, $EtNO_2$, 1-$PrNO_2$, and 2-$PrNO_2$), alkenes (C_2H_4, C_3H_6) and CO were formed as minor products at lower temperatures (350–450°C). When the reaction temperature was raised above 450°C, the selectivities to oxygenates decreased and

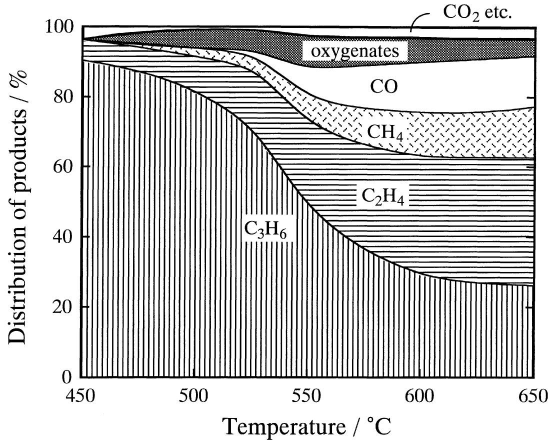

Fig. 2. Effects of temperature on the distribution of products for the oxidation of C_3H_8 with O_2.

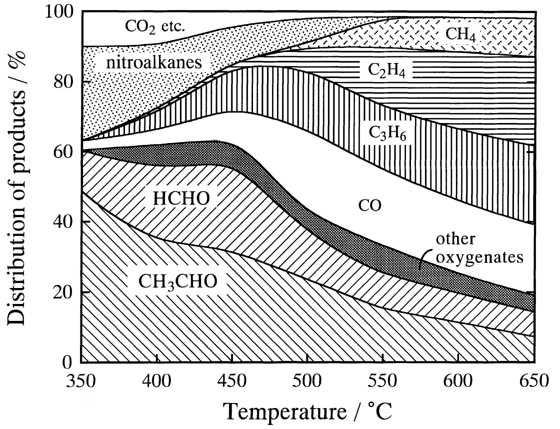

Fig. 3. Effects of temperature on the distribution of products for the oxidation of C_3H_8 with $(NO+O_2)$.

nitroalkanes disappeared at >550°C. In contrast, the selectivities to alkenes (C_3H_6, C_2H_4), CH_4 and CO increased considerably at >550°C. This large difference in the product distributions between Figs. 2 and 3 suggests that the reaction mechanism for oxidation of C_3H_8 with $(NO+O_2)$ is quite different from the non-catalytic auto-oxidation mechanism.

Fig. 4 shows the effects of temperatures on the yield of the sum of oxygenates for the oxidations of CH_4, C_2H_6, and C_3H_8 with $(NO+O_2)$ and with O_2. The product distributions in oxygenates were roughly as HCHO≫MeOH>MeCHO for oxidation of C_2H_6, and as HCHO≫MeOH for oxidation of CH_4. The yields of the sum of oxygenates for the oxidations of CH_4, C_2H_6 and C_3H_8 with $(NO+O_2)$ were remarkably higher than those with O_2 at all temperatures. Especially, dramatic enhancements in the selectivity to oxygenates were observed by the addition of NO at low temperature region, 350–500°C.

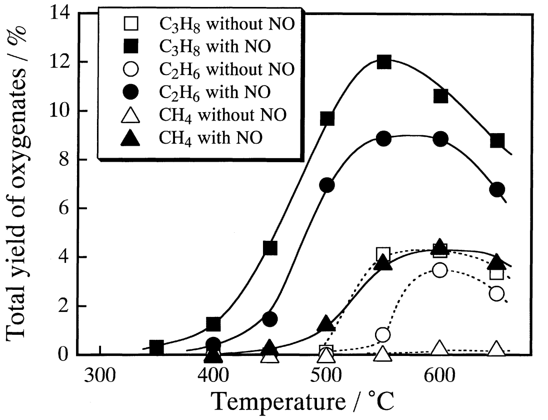

Fig. 4. Effect of the addition of NO on the yields of oxygenates for the oxidations of CH_4, C_2H_6, and C_3H_8 with O_2.

Fig. 5 shows the effects of partial pressure of NO on the formation rates of products for oxidation of C_3H_8 with $(NO+O_2)$ at 420°C (low temperature region). The formation rates of each product increased with increasing P(NO).

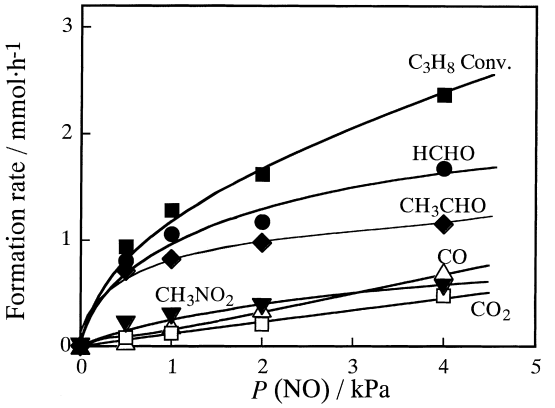

Fig. 5. Effect of P(NO) on the formation rates of products for the oxidation of C_3H_8 with O_2 at 420°C. $P(C_3H_8)$ 20 kPa, $P(O_2)$ 10 kPa, flow rate 120 ml min^{-1}.

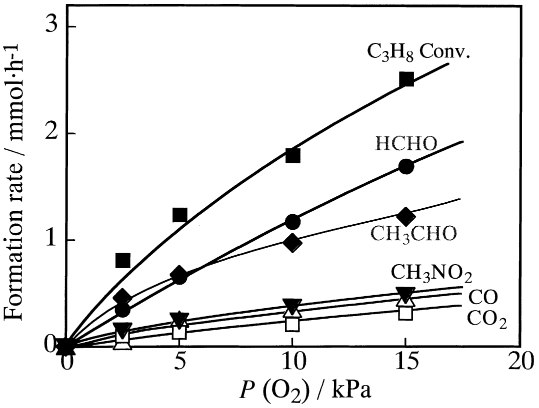

Fig. 6. Effect of $P(O_2)$ on the formation rates of products for the oxidation of C_3H_8 at 420°C. $P(C_3H_8)$ 20 kPa, P(NO) 2 kPa, flow rate 120 ml min^{-1}.

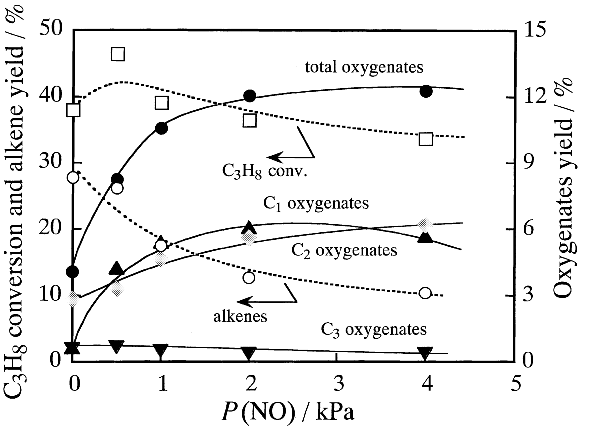

Fig. 7. Effect of P(NO) on the oxidation of C_3H_8 at 550°C. $P(C_3H_8)$ 20 kPa, $P(O_2)$ 10 kPa, flow rate 120 ml min^{-1}.

Fig. 6 shows the effects of $P(O_2)$ on the formation rates of each product at 420°C. The formation rates of each products increased with a rise in $P(O_2)$.

Fig. 7 shows the effects of P(NO) on the conversion of C_3H_8 and on the yields of products at 550°C. It should be recalled that the oxidation of C_3H_8 in high temperature region (>500°C) proceeded in the absence of NO (Fig. 1). The conversion of C_3H_8 in Fig. 7 did not change appreciably with increasing P(NO) mainly due to complete consumption of O_2. However, the selectivities to oxygenates increased and those to C_3H_6 and C_2H_4 decreased with increasing P(NO). These results suggest that reaction mechanism for the formation of products were changed dramatically by addition of NO also at high temperature region.

Optimum reaction conditions for the formation of oxygenates were examined for the oxidations of CH_4, C_2H_6, C_3H_8 and iso-C_4H_{10}. The results are shown in Table 2. Fairly good yields of the sum of oxygenates were obtained for each light alkane under the reaction conditions in Table 2. Under these conditions, only a trace of nitroalkanes and N_2 was observed. Therefore, most of the NO introduced was remained in the gas mixture at the outlet. This observation indicates that NO can be recycled as catalyst for the oxidation of light alkanes.

As described above, co-addition of NO and O_2 remarkably accelerated the rate of conversion of light alkanes and the formation rates of oxygenates. The reaction between NO and alkanes did not take place in the absence of O_2. These observations suggest that NO_2 would work as an initiator or an active oxidant in the oxidations. Thus, it is speculated that some NO_2-containing hydrocarbons could be the reaction intermediate for the formation of oxygenates. In fact, small amounts of nitroalkanes ($MeNO_2$, $EtNO_2$ and $PrNO_2$)

Table 2
Yields of oxygenates under optimum conditions

Reactant	Temparature (°C)	Pressure (kPa)			Conversion (%)	Yield (based on the alkanes reacted) (%)				
		Alkane	O_2	NO		HCHO	MeOH	MeCHO	Acetone	Total
CH_4[a]	600	5.0	2.5	0.5	17	6.5	0.2	—	—	6.7
C_2H_6[a]	600	5.0	2.5	0.5	31	9.5	0.8	1.0	—	11.3
C_3H_8[a]	550	10	5.0	1.0	38	5.6	1.8	5.3	0.2	12.9
iso-C_4H_{10}[b]	425	10	15	4.0	53	5.6	1.2	3.7	18.2	28.7

[a] Flow rate=120 ml min^{-1}.
[b] Flow rate=60 min^{-1}.

Table 3
Decomposition of *tert*-BuONO at 400°C

Conditions	Conversion (%)	Formation rate (μmol min^{-1})				
		Acetone	HCHO	CO	CO_2	CH_3NO_2
He	82	26	trace	0	0.1	1.0
O_2	100	29	8.0	51	6.4	4.8
O_2+NO	100	27	8.8	59	3.2	6.0

Reaction conditions: P(*tert*-BuONO)=1.1 kPa, P(O_2) 10 kPa, P(NO) 1.0 kPa, flow rate 60 ml min^{-1} (balanced with He).

were formed at low temperatures as shown in Fig. 3. Therefore, decomposition reactions of 1-$PrNO_2$ and 2-$PrNO_2$ were carried out to get information about the reaction mechanisms. The results showed that the major product was C_3H_6 in both cases. This result suggests that nitroalkane could not be the precursor for the formation of oxygenates.

Table 3 shows the results of the decomposition of *tert*-BuONO. The decomposition of *tert*-BuONO in a stream of He at 400°C produced acetone as main products, but a deposition of carbon on the wall of reactor was observed. When O_2 or a mixture of NO and O_2 was added, the formation rate of acetone was not changed but the formation of HCHO, CO, CO_2 and CH_3NO_2 were observed instead of the carbon deposition. These results strongly suggest that alkyl nitrite could be the reaction intermediate for the formation of oxygenates in the oxidation of light hydrocarbons with (NO and O_2).

On the bases of the results in this work together with the mechanism suggested for the radical-chain auto-oxidation [8,9], we propose Scheme 1 for the oxidation of light alkanes catalysed by NO. NO_2 is an initiator for the formation of alkyl radicals (Eq. 2). The alkyl radicals (R•) reacts with NO_2 producing RONO as an reaction intermediate for the formation of oxygenates (Eq. 3). Then, RONO decomposes to RO• regenerating NO (Eq. 4). RO• decomposes to aldehydes or acetone (Eqs. 5, 5′, 5″) and CH_3• which is further oxidized into HCHO, CO and CO_2 (Eq. 6). RNO_2 formed in Eq. 3′ may decompose into alkenes and CO.

$$\mathrm{NO} + 1/2\,\mathrm{O_2} \longrightarrow \mathrm{NO_2} \tag{1}$$

$$\mathrm{RH} + \mathrm{NO_2} \longrightarrow \mathrm{R\cdot} + \mathrm{HNO_2} \tag{2}$$

$$\mathrm{R\cdot} + \mathrm{NO_2} \longrightarrow \mathrm{RONO} \tag{3}$$

$$\mathrm{R\cdot} + \mathrm{NO_2} \longrightarrow \mathrm{RNO_2} \tag{3'}$$

$$\mathrm{RONO} \longrightarrow \mathrm{RO\cdot} + \mathrm{NO} \tag{4}$$

$$\mathrm{RO\cdot} \longrightarrow \mathrm{HCHO} + \mathrm{R'\cdot} \quad (\mathrm{R} = \mathrm{CH_3}, \mathrm{C_2H_5}, \text{n-}\mathrm{C_3H_7}) \tag{5}$$

$$\mathrm{RO\cdot} \longrightarrow \mathrm{CH_3CHO} + \mathrm{CH_3\cdot} \quad (\mathrm{R} = iso\text{-}\mathrm{C_3H_7}) \tag{5'}$$

$$\mathrm{RO\cdot} \longrightarrow \mathrm{CH_3COCH_3} + \mathrm{CH_3\cdot} \quad (\mathrm{R} = tert\text{-}\mathrm{C_4H_9}) \tag{5''}$$

$$\mathrm{CH_3\cdot} \xrightarrow{\mathrm{O_2},\ \mathrm{NO_2}} \mathrm{HCHO, CO, CO_2} \tag{6}$$

Scheme 1.

On the other hand, it is reasonable to assume that for the oxidations of light alkanes with O_2 in the absence of NO proceed through the radical-chain auto-oxidation mechanism in Scheme 2. Peroxy–alkyl radicals work as intermediates for the oxidation of light alkanes (Eqs. 7 and 8). In this mechanism, alkenes are produced as the main products of the oxidation (Eqs. 9 and 10) as in fact observed in Fig. 2.

In the case of the catalytic oxidation of alkanes by NO at low temperature region, the oxidation proceed through Scheme 1. While, we cannot neglect the contribution of Scheme 2 for the oxidation with NO and O_2 at high temperature region.

$$\mathrm{RH} + \mathrm{O_2} \longrightarrow \mathrm{R\cdot} + \mathrm{HO_2\cdot} \tag{7}$$

$$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{RO_2\cdot} \tag{8}$$

$$\mathrm{RO_2\cdot} \longrightarrow \text{alkene} + \mathrm{HO_2\cdot} \tag{9}$$

$$\mathrm{RO_2\cdot} \longrightarrow \mathrm{R'CHO} + \mathrm{HO\cdot} \tag{9'}$$

$$\mathrm{R\cdot} \longrightarrow \text{alkene} + \mathrm{H\cdot} \tag{10}$$

Scheme 2.

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