

Partial oxidation of methane with N_2O over $\text{Fe}_2(\text{MoO}_4)_3$ catalyst

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Received 9 August 1993; accepted 23 October 1993

The product distributions for partial oxidation of methane on $\text{Fe}_2(\text{MoO}_4)_3$ catalyst were changed remarkably when the oxidant was switched from oxygen to nitrous oxide. When oxygen was used as the oxidant, the main products were HCHO and CO. However, when nitrous oxide was used, the formation of HCHO was greatly suppressed and C_2 hydrocarbons (C_2H_6 and C_2H_4) were newly produced. The difference in kinetic behaviors between the two reactions using nitrous oxide and oxygen as the oxidant can be explained in terms of the competitive conversions of methyl intermediate into HCHO and C_2H_6 . In the case of nitrous oxide as the oxidant, the adsorbed methyl intermediate would be transformed predominantly into C_2H_6 due to a low steady-state concentration of the active oxygen species on $\text{Fe}_2(\text{MoO}_4)_3$.

Keywords: Methane; partial oxidation; nitrous oxide; iron molybdate

1. Introduction

The direct conversion of methane into more valuable products, especially into oxygenates such as methanol and formaldehyde, is a great challenge in catalysis. Several researchers [1–3] have reported that methanol and formaldehyde can be synthesized on molybdena catalysts supported on silica when nitrous oxide is used as the oxidant. There are some reports for the oxidation of methane using oxygen on molybdenum-based catalysts [3–5]. Barbaux et al. [3] have reported that only total oxidation of methane occurs in the presence of oxygen as the oxidant. Spencer et al. [4] have obtained formaldehyde but only with a selectivity of about 30% at a 5% methane conversion, which is notably lower than those reported using nitrous oxide. Moreover, no methanol was obtained. Thus, the oxidant may drastically change the reaction sequence in partial oxidation of methane to oxygenates.

There are several papers describing the kinetic and mechanistic differences between the oxidative coupling of methane using oxygen and nitrous oxide [6,7]. However, for partial oxidation of methane to oxygenates, the reports concerning this kind of study are very scarce.

Schwank and coworkers [5] have reported a surprisingly high yield of formaldehyde (23%) for partial oxidation of methane using oxygen over iron molybdate catalysts. Although we could not reproduce such a high HCHO yield, we have confirmed that $\text{Fe}_2(\text{MoO}_4)_3$ is an effective catalyst for partial oxidation of methane to formaldehyde when oxygen is used as the oxidant [8,9]. We have proposed an Eley–Rideal type reaction mechanism where the rate-determining step is the activation of methane by the dissociatively adsorbed oxygen [8,9]. In order to clarify this reaction mechanism in more detail, we have studied the partial oxidation of methane over $\text{Fe}_2(\text{MoO}_4)_3$ using nitrous oxide as the oxidant in this work. The role of oxidant will be discussed by comparing the kinetic studies on the reactions using nitrous oxide and oxygen.

2. Experimental

$\text{Fe}_2(\text{MoO}_4)_3$ catalyst was prepared using a precipitation method by adding the aqueous solution of iron nitrate to that of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. The resulting precipitate was dried at 373 K, calcined at 673 K for 6 h and subsequently at 1023 K for 2 h in air.

The catalytic reactions were carried out under atmospheric pressure using a conventional flow system with a fixed-bed quartz reactor. The details about the reactor design and experimental procedure have been described elsewhere [9]. The gases used in this study were He (>99.9%), CH_4 (>99.97%), N_2O (>99.9%) and O_2 (99%). These were used without further purification. The products were analyzed by on-line gas chromatography. The rates of CH_4 and N_2O conversions were calculated on the basis of the amount of the total carbon products (C_2H_6 , C_2H_4 , HCHO, CO and CO_2) and that of N_2 produced, respectively. The carbon balance between the feed and the effluent gas was better than 95%.

3. Results and discussion

3.1. COMPARISON OF CATALYTIC RESULTS USING DIFFERENT OXIDANTS

Table 1 shows typical examples of the results for oxidations of methane with N_2O and O_2 on $\text{Fe}_2(\text{MoO}_4)_3$ catalyst under the same reaction conditions. When oxygen was used as the oxidant, HCHO and CO were the main products. A small amount of CO_2 and a trace of CH_3OH (selectivity <0.1%) were also detected. However, C_2 hydrocarbons ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) were not produced at all. This was true under different reaction conditions applied in this work [8,9]. In contrast with this, C_2 hydrocarbons ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) became the predominant products when N_2O was used instead of O_2 . This observation is quite unexpected from the results reported so far [1–3], because N_2O has been believed to be a better oxidant than O_2

Table 1

Comparison of catalytic results for oxidation of CH₄ with different oxidants ^a

Oxidant	CH ₄ conversion (%)	Selectivity (%)				
		HCHO	C ₂ H ₆	C ₂ H ₄	CO	CO ₂
O ₂	2.60	49.2	0	0	47.7	3.1
N ₂ O	1.61	23.0	39.8	6.2	27.3	3.7

^a Reaction conditions: $T = 998$ K, $W = 0.5$ g, $F_{\text{total}} = 3.6$ dm³/h, $P(\text{CH}_4) = P(\text{oxidant}) = 25.3$ kPa. The total pressure of the feed gas was balanced with He to 101.3 kPa.

for the partial oxidation of CH₄ to oxygenates over molybdenum based oxides. To understand the role of the different oxidants in the overall reaction paths, we have carried out detailed kinetic studies for the oxidations of methane using N₂O and O₂ as below.

3.2. REACTION PATHWAYS

In order to obtain information about the reaction pathways, the changes in the product distributions with contact time have been observed for the oxidation of methane using N₂O at 973 and 998 K. As shown in fig. 1, the CH₄ conversion increased linearly with the contact time (expressed as W/F) at 973 K. The HCHO yield also increased linearly with the contact time, but the increase in the yield of C₂ (C₂H₆ and C₂H₄) obviously slowed down at longer contact time. In contrast with this deceleration of the increase in C₂ yield, the CO yield increased more steep-

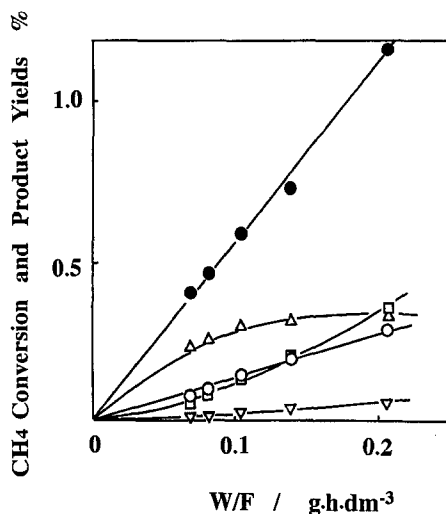
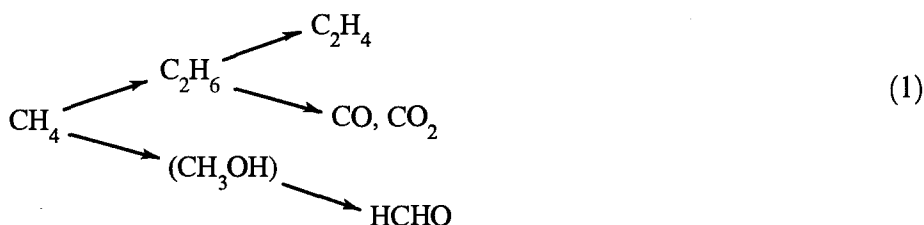


Fig. 1. CH₄ conversion and product yields as a function of the contact time at 973 K. (●) CH₄ conversion, (○) HCHO yield, (△) C₂ yield, (□) CO yield, (▽) CO₂ yield. $P(\text{CH}_4) = P(\text{N}_2\text{O}) = 25$ kPa, $W = 0.5$ g.

ly at longer contact time. The change of the product selectivities at 973 K is shown in fig. 2. The HCHO selectivity and the sum of the selectivities of C_2 , CO and CO_2 are almost constant with the change in contact time. These results suggest that HCHO is formed in parallel with other products, namely, C_2H_6 , C_2H_4 and carbon oxides (CO and CO_2). The observation that the selectivities of carbon oxides increase with a decrease in the selectivity of C_2 hydrocarbons (mainly C_2H_6) suggests that carbon oxides are the consecutive products from C_2H_6 . Similar results to those in figs. 1 and 2 have also been obtained at 948 and 998 K.

As a summary, the pathways for partial oxidation of CH_4 by N_2O over $Fe_2(MoO_4)_3$ can be written as



Though methanol was formed only with a trace amount, we cannot exclude the possibility that CH_3OH is the precursor of HCHO. In fact, the results of the oxidation of methanol by N_2O over $Fe_2(MoO_4)_3$ under similar reaction conditions showed that methanol was very easily transformed to HCHO.

The reaction pathways in eq. (1) are to be considered only when N_2O is used as

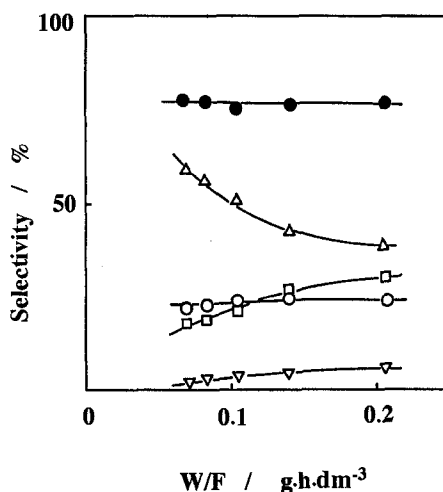


Fig. 2. Product selectivities as a function of the contact time at 973 K. (○) HCHO, (△) C_2 , (□) CO, (▽) CO_2 , (●) $C_2 + CO + CO_2$.

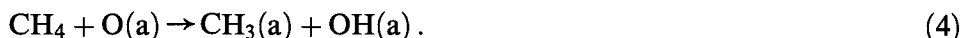
an oxidant. We have proposed that the reaction using O₂ over the same catalyst proceeds as follows [8,9]:



It is to be noted that, when N₂O is used as the oxidant, C₂H₆ is formed as one of the primary products, and thus the product distributions in two cases are notably different as shown in table 1.

3.3. KINETIC FEATURES AND MECHANISTIC MODELS

Figs. 3 and 4 show the dependences of the rate of CH₄ conversion ($r(\text{CH}_4)$) upon CH₄ and N₂O partial pressures, respectively. These curves indicate that the rate of CH₄ conversion depends on the pressures of N₂O and CH₄ by less than first order for each reactant. In the case of the reaction using O₂ as the oxidant, very good linear correlation was obtained between the rate of CH₄ conversion and the partial pressure of CH₄ under similar reaction conditions [9]. We have suggested a Rideal–Eley model for the reaction of methane with oxygen, i.e., CH₄ is activated by the dissociatively adsorbed oxygen as shown in the following reactions:



Reaction (4) has been postulated as the rate-determining step. Therefore, it is reasonable to consider that CH₄ is activated in the similar way when N₂O is used as the oxidant, i.e., CH₄ is activated by the active oxygen species generated from the decomposition of N₂O as follows:

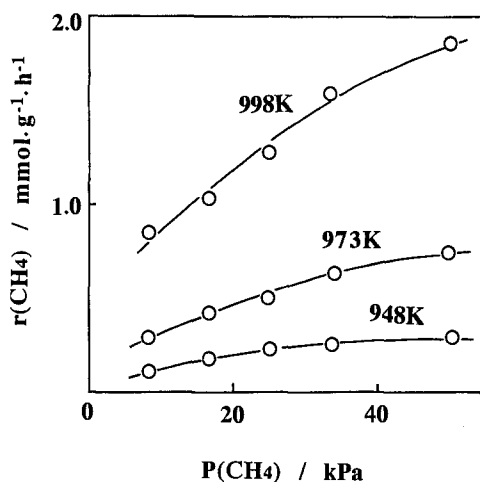


Fig. 3. The rate of CH₄ conversion versus partial pressure of CH₄. $P(\text{N}_2\text{O}) = 25 \text{ kPa}$, $F_{\text{total}} = 3.6 \text{ dm}^3/\text{h}$, $W = 0.5 \text{ g}$.

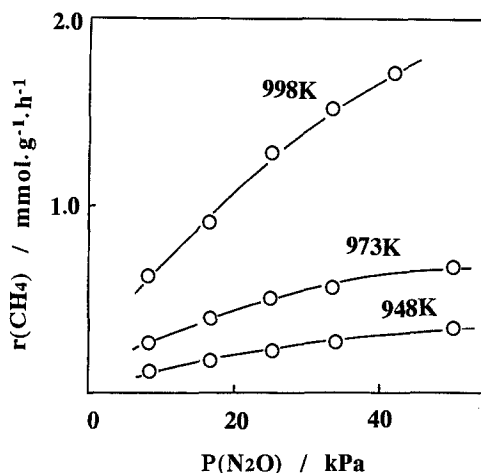


Fig. 4. The rate of CH_4 conversion versus partial pressure of N_2O . $P(CH_4) = 25$ kPa, $F_{total} = 3.6$ dm³/h, $W = 0.5$ g.



However, if reaction (4) is also the rate-determining step in the case of the oxidation using N_2O , the rate of methane conversion should be proportional to the partial pressure of methane as this was the case in the oxidation by O_2 . Therefore, the results in fig. 3 require some modifications of this simple reaction model. Let us hypothesize here that, in contrast with the very fast reaction (3), the rate of active oxygen formation from N_2O (reaction (5)) is not so fast compared to the rate of reaction (4). In order to confirm this speculation, we have investigated the decomposition reaction of N_2O on the same catalyst. Fig. 5 shows the rate of conversion of N_2O in the presence and absence of CH_4 as functions of temperature. The results indicate that the rate of conversion of N_2O is accelerated considerably in the presence of methane. Moreover, gaseous oxygen was not observed during the conversion of N_2O in the presence of CH_4 . These results strongly suggest that reaction (5) is not so fast compared to reaction (4). However, reaction (5) cannot be the rate-determining step in the oxidation of methane because the rate of methane conversion depends on the partial pressure of methane and the rate is not proportional to the pressure of N_2O (fig. 4).

It may be reasonable to assume that the surface $O(a)$ species is mainly consumed in the reaction with methane because no gaseous oxygen is formed during the reaction and the CH_4 conversion is always kept at low level ($< 2\%$ in kinetic studies). By steady-state assumption for the surface concentration of $O(a)$, the rate of CH_4 conversion can be induced as below.

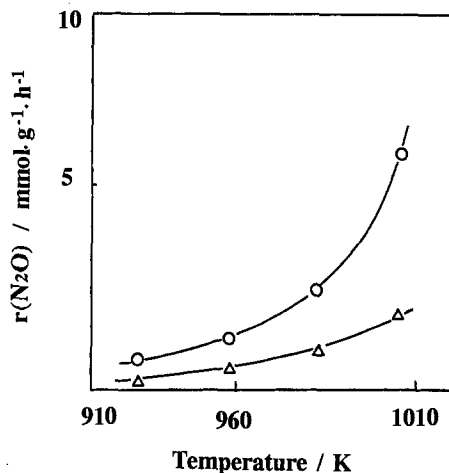


Fig. 5. The rate of N_2O decomposition versus reaction temperature in the absence (Δ) and presence (\circ) of CH_4 ($P(CH_4) = 25$ kPa). $F_{total} = 3.6$ dm³/h, $W = 0.5$ g, $P(N_2O) = 25$ kPa.

$$\frac{d[O(a)]}{dt} = k_5 P(N_2O)(n - [O(a)]) - k_4 P(CH_4)[O(a)] = 0, \quad (6)$$

where n is the total concentration of active sites on the catalyst surface. Hence,

$$[O(a)] = \frac{nk_5 P(N_2O)}{k_5 P(N_2O) + k_4 P(CH_4)} \quad (7)$$

and thus

$$r(CH_4) = k_4 P(CH_4) \frac{nk_5 P(N_2O)}{k_5 P(N_2O) + k_4 P(CH_4)}. \quad (8)$$

We have examined whether the kinetic results shown in figs. 3 and 4 can be fitted to this equation by plotting $1/r(CH_4)$ against $1/P(CH_4)$ at constant N_2O partial pressure and against $1/P(N_2O)$ at constant CH_4 partial pressure, respectively. Good linear correlations as shown in figs. 6 and 7 would support the model suggested above. Furthermore, we can calculate the value of k_5/k_4 from the ratio of the slope and the intercepts of the straight lines in figs. 6 and 7. The values calculated from both figures are in good agreement with each other as shown in table 2. The ratio of k_5/k_4 is close to unity at 948 K, and it decreases with increasing temperature. This result implies that the activation energy of reaction (5) is lower than that of reaction (4).

3.4. THE FORMATION OF PRODUCTS

As described above, the rate of production of active oxygen from N_2O is comparable to that of the consumption of the oxygen by methane. This must be responsi-

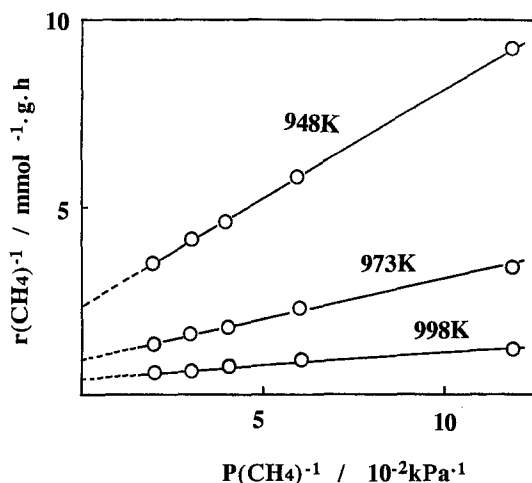


Fig. 6. $1/r(\text{CH}_4)$ versus $1/P(\text{CH}_4)$. The reaction conditions are the same as shown in fig. 3.

ble for the difference in the product distributions between the oxidations of methane using O_2 and N_2O . In the case of O_2 , as we suggested previously [8], the dissociative adsorption (eq. (3)) must be very fast and in equilibrium. Moreover, adsorbed dioxygen species may also exist on the surface. Therefore, the intermediate CH_3 species could instantly be transformed to CH_3OH and consequently to HCHO by these oxygen species as follows:

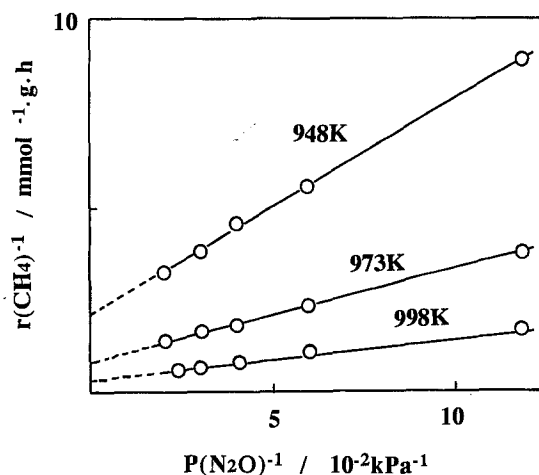


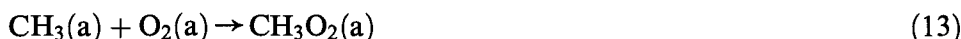
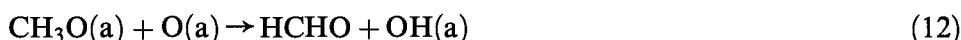
Fig. 7. $1/r(\text{CH}_4)$ versus $1/P(\text{N}_2\text{O})$. The reaction conditions are the same as shown in fig. 4.

Table 2

 k_5/k_4 calculated from figs. 6 and 7^a

Temperature (K)	k_5/k_4	
	from fig. 6	from fig. 7
948	0.98	0.94
973	0.87	0.81
998	0.74	0.74

^a Reaction conditions: $F_{\text{total}} = 3.6 \text{ dm}^3/\text{h}$, $W = 0.5 \text{ g}$, $P(\text{CH}_4) = P(\text{N}_2\text{O}) = 25.3 \text{ kPa}$. The total pressure of the feed gas was balanced with He to 101.3 kPa.



However, in the case of N₂O, the concentration of active oxygen species is not high enough to transform all the CH₃ species into oxygenates. Therefore, the selectivity to HCHO is lowered, but most of the CH₃ species are allowed to couple to give C₂H₆ as one of the primary products. Further oxidation of C₂H₆ with the active oxygen may produce C₂H₄, CO and CO₂.

As described earlier, the formation of carbon oxides (CO and CO₂) via oxidation of HCHO can be neglected under the reaction conditions in this work (eq. (1)). However, the carbon oxides are formed through the oxidation of HCHO when O₂ is used as the oxidant (eq. (2)). This discrepancy can be explained in terms of the preferential oxidation of C₂H₆ by the surface active oxygen. In the presence of gaseous oxygen, however, the CH₃ intermediate is immediately converted to HCHO (through CH₃O(a) or CH₃OH) and further oxidation of HCHO by dioxygen must be responsible for the formation of carbon oxides.

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