High Yield Methanol Formation in a CH_4-O_2-NO_2 Gaseous Selective Oxidation at 1 atm

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Methanol and formaldehyde except for carbon oxides, nitromethane, and formic acid were obtained with high selectivities at 808K under 1 atm in a gaseous reaction of 55.6CH_4-27.7O_2-0.5NO_2-16.2He. Selectivities to methanol and formaldehyde were 27.3% and 24.5% at the level of 10% methane conversion, respectively. The reaction route to methanol formation was addressed.

Light alkane selective oxidation with oxygen is desirable for the effective utilization of natural gas resources. In recent years, many researchers have studied the selective oxidation of natural gas with various types of catalysts. However, methanol yield is still low because of the successive oxidation to CO and CO_2.[1-3] Formation of methanol from methane and oxygen in a gaseous reaction has been also reported,[2,4-11] however, most of those reactions have been carried out under a high pressure. Initiators and sensitizers for a radical chain reaction have been also examined.[12,13] Promotion effect of nitrogen oxides for methane selective oxidation in a gaseous reaction has been reported, though the main product of the reaction is formaldehyde and the methanol yield is very low.[14-20] Very recently, Banares et al.[20] obtained a high yield of methanol at 883K with a V_2O_5/SiO_2 catalyst in the presence of NO. In this study, we will report the promotion effects of NO_2 for methanol formation in CH_4-O_2 gaseous reaction without a catalyst at 1 atm, and discuss the role of NO_2.

The standard reaction was carried out with using a test gas (CH_4: 55.6%, O_2: 27.7%, NO_2: 0.5%, He: 16.2%). Total flow rate was 120ml·min^{-1}. Concentration of NO_2 was changed from 0.125 to 1.0%. The ratio of CH_4 to O_2 was kept as 2:1 in every test. Quartz tube (7 mm i.d.) was used and the length of heated reaction zone was 200 mm. Products were analyzed with two gas chromatographs. Carbon balance before and after the reaction exceeded 95%. Measurements were carried out after the reaction for 30 min at each condition and all experimental data are taken at least three times for the check of their reproducibility.

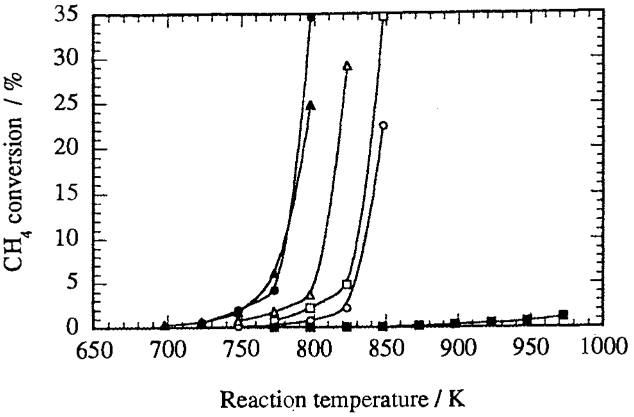

Figure 1. Effects of NO_2 addition on CH_4 conversion as a function of reaction temperature. 0% (■), 0.125% (○), 0.25% (□), 0.5% (△), 0.75% (●), and 1.0% (▲). Reaction gas: 55.6%CH_4 + 27.7%O_2 +NO_2 in He. Flow rate: 120 ml•min^{-1}, SV: 936h^{-1}.

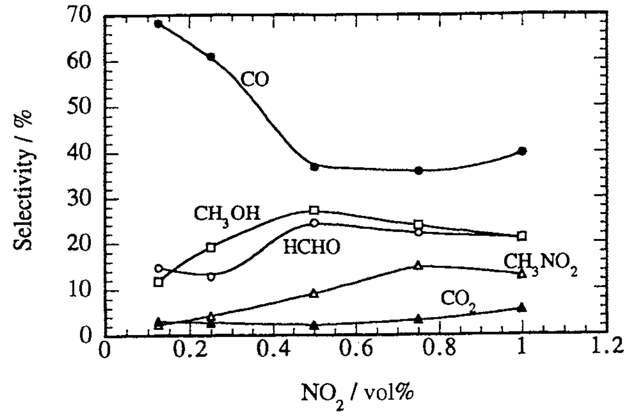

Figure 2. Selectivity to each product as a function of NO_2 concentration at 10% CH_4 conversion. CO (●), CH_3OH (□), HCHO (○), CH_3NO_2(△), and CO_2 (▲). Reaction condition is the same as shown in Figure 1.

CH_4 conversion is shown in Figure 1. The conversion without NO_2 is quite low even at 966K. The addition of a small quantity of NO_2 in the reaction gas enhances the conversion greatly. The addition of 1% NO_2 in the reaction gas lowered the reaction temperature more than 230 degree at the level of 1% conversion. Methanol, formaldehyde, CO, CO_2, nitromethane and the trace of formic acid were observed in the products. The measurment of hydrogen was not carried out. Selectivities to every product under several NO_2 concentrations for the level at the 10% methane conversion are shown in Figure 2. In the range of 0.125-0.5% NO_2 concentration, the selectivities of methanol and formaldehyde increase and decrease slightly in the excess region than 0.5%. The highest selectivities to methanol and formaldehyde are obtained at 0.5% NO_2. It is worthy notice that the selectivity to methanol is higher than that of formaldehyde. NO_2 addition promotes both the conversion and the selectivities to C_1-oxygenates. The slight decrease of C_1-oxygenates at a higher NO_2 concentration is probably due to the destruction of those.

The effects of NO addition should not be ignored because of the equilibrium reaction between NO_2 and NO in the presence of O_2. When 1.0% NO instead of NO_2 was fed into the reaction gas, CH_4 conversion was lowered and formation of C_1-

oxygenates was observed. The reaction temperature was 30 degree higher than that of NO_2 as compared with the same concentration of NO_2 at the level of 10% conversion. Selectivities to C_1-oxygenates, especially methanol was slightly lower than the case of NO_2. Since the oxidation rate from NO to NO_2 is fairly low under such a low level NO concentration at 800K,[21] most of NO seems to keep itself at the initial region of the reactor. Since the rate-determining step in a methane selective oxidation is the abstraction of hydrogen from methane, we therefore assure the addition of NO_2 is more favorable to abstracting hydrogen from methane than that of NO in the feed gas.

Nitromethane is detected from the products. The formation of nitromethane during the selective oxidation of CH_4-O_2-NOx has not been reported except for the reaction at 3 atm by Han et al.[18] As shown in Figure 2, the added NO_2 reacted to nitromethane. The proportion of nitromethane to initial NO_2 was ca 1.0 in the range of 0.125-0.75%NO_2. The ratio decreased to 0.57 with 1.0% addition of NO_2.

About the reaction mechanism in the selective oxidation of CH_4-O_2-NO_2, the abstraction of hydrogen by NO_2 from methane has been suggested widely,[17,19] and confirmed by theoretical calculation.[22] In CH_4-O_2, it has been proposed that after the abstraction of hydrogen from CH_4, CH_3O_2 is produced easily between CH_3 and O_2, then CH_3O is formed from CH_3O_2 as follows.[1-4]

$$CH_3OO + CH_4 \rightarrow CH_3OOH + CH_3 \tag{1}$$

$$CH_3OOH \rightarrow CH_3O + OH \tag{2}$$

However, the formation of CH_3O from CH_3O_2 needs a high energy.[4] Therefore the process from CH_3O_2 to CH_3O is important. In CH_4-O_2-NOx, it is reported that the activation energy of CH_3O formation from NO and CH_3OO, or that from NO_2 and CH_3 is much lower than that of Eqs. (1) and (2) for CH_3O formation without NOx.[22] On the base of our experimental results and these references, we consider that the presence of NO_2 promoted both the hydrogen abstraction from methane and the formation of CH_3O shown as below.

$$CH_4 + NO_2 \rightarrow CH_3 + HNO_2 \tag{3}$$

$$CH_3 + NO_2 \rightarrow CH_3O + NO \tag{4}$$

$$CH_3 + O_2 \rightarrow CH_3OO \tag{5}$$

$$CH_3OO + NO \rightarrow CH_3O + NO_2 \tag{6}$$

Since the amount of activated methane in the reaction was higher than that of added NO_2, we assumed that NO_2 reacted with CH_4 over and over in a higher temperature region. Therefor HNO_2 in Eq. (3) must be decomposed to NO_2.

C_1-oxygenates can be produced by reactions shown as follows.

$$CH_3O + CH_4 \rightarrow CH_3OH + CH_3 \tag{7}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{8}$$

For successive oxidation of methanol and formaldehyde, it was reported that OH played an important role[4].

$$CH_3OH + OH \rightarrow CH_2OH + H_2O \tag{9}$$

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \tag{10}$$

$$CH_2O + OH \rightarrow CHO + H_2O \tag{11}$$

$$CHO + O_2 \rightarrow CO + HO_2 \tag{12}$$

In the presence of NO_2, the depression of Eqs. (1) and (2) by the substitution of Eqs. (4) and (6) led to the decrease of OH, and this decrease of OH in the gas phase brings the decline of decomposition of methanol and formaldehyde. Therefore, we detected the increases of C_1-oxygenates in Fig. 2 in the presence of NO_2. The selectivity of CH_3OH is higher than that of CH_2O as shown in Fig.2. Therefore it is plausible that lower yield of formaldehyde is due to its easily decomposition in Eq. (11) as comparison with that of methanol in Eq. (9).[4]

Reaction conditions such as dilution, ratio of methane to oxygen, etc will effect on the selectivity of C_1-oxygenates in CH_4-O_2-NO_2. The more distinct reaction pathways will be needed to discuss.

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