Simultaneous removal of N_2O and CH_4 as the strong greenhouse-effect gases over Fe-BEA zeolite in the presence of excess O_2

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Simultaneous catalytic removal of N_2O and CH_4 as the strong greenhouse-effect gases was found to be possible over an Fe-ion-exchanged BEA zeolite (Fe-BEA) by the selective catalytic reduction (SCR) of N_2O with CH_4. The direct decomposition of N_2O ($2N_2O \rightarrow 2N_2 + O_2$) and the oxidation of CH_4 ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$) over Fe-BEA zeolite required high temperature above 400 and 450 °C, respectively. Nevertheless, the catalytic reduction of N_2O by adding CH_4 over Fe-BEA zeolite readily occurred at much lower temperatures (ca. 250–350 °C) whether in the presence of O_2 or not. No oxidation of CH_4 by O_2 took place at these temperatures. On the basis of these results and the kinetic studies, it was concluded that CH_4 reacted selectively with N_2O to produce N_2, CO_2 and H_2O over Fe-BEA zeolite even in the presence of excess O_2. Overall stoichiometry of the SCR of N_2O with CH_4 was determined as follows: $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$.

Keywords: SCR of N_2O, CH_4, greenhouse-effect gas, simultaneous removal, Fe-BEA zeolite

1. Introduction

Nitrous oxide (N_2O) and methane (CH_4) are strong greenhouse-effect gases with a global warming potential (GWP) per molecule of about 300 and 30 times that of carbon dioxide (CO_2), respectively [1]. N_2O is also identified as a contributor to the destruction of ozone in the stratosphere [2]. From the point of view of environment, therefore, it is interesting that a selective catalytic reduction (SCR) of N_2O by CH_4 is applied to simultaneous removal of N_2O and CH_4 in the emission gases. Recently, we reported that the SCR of N_2O by CH_4 took place effectively over an Fe-ion-exchanged BEA zeolite (Fe-BEA) below 400 °C even in the presence of excess oxygen [3]. The Fe-BEA zeolite was more active for this reaction than Fe-MFI and Co-MFI reported in the literature [4,5]. The SCR of N_2O with CH_4 readily proceeded at much lower temperatures, compared with the direct decomposition of N_2O ($2N_2O \rightarrow 2N_2 + O_2$). However, fundamental issues in the SCR of N_2O with CH_4 over the Fe-BEA zeolite such as the overall stoichiometry and the kinetics parameters (i.e., apparent activation energies, reaction orders) in the presence or in the absence of O_2 have not been elucidated so far. In this work, we examined the difference in the stoichiometry and the kinetics in the aforementioned reaction between the presence of O_2 and the absence of O_2.

2. Experimental

Fe-BEA ($SiO_2/Al_2O_3 = 27.3$) catalyst was prepared by ion-exchange with a dilute solution of $FeSO_4$ at 50 °C for 20 h under nitrogen atmosphere, and calcined in air for 12 h at 500 °C [3]. The zeolite support (H-BEA) was supplied by TOSOH Co. The loading weight of Fe on BEA support was 0.77 wt% (25% exchanged with Fe^{2+}, 1.3×10^{-4} mol-Fe-ion g-cat^{-1}). The reaction was carried out in a standard fixed-bed flow reactor by passing a gaseous mixture of N_2O (0–2000 ppm), CH_4 (0–500 ppm) and O_2 (0–10%) in He flow at a total flow rate of 50 $cm^3\,min^{-1}$ over 50 mg of catalyst (total pressure 1 atm, space velocity (SV) 60 000 h^{-1}). The sample was pretreated at 500 °C with O_2 for 1 h in a flow reactor, followed by a He purge at the initial reaction temperature. The products were monitored by an on-line gas chromatograph (Shimadzu GC-8A) equipped with Molecular Sieve 5A (N_2, CH_4, CO) and Porapak Q (N_2O, CO_2, H_2O). The catalytic activity for the reduction of N_2O with CH_4 was evaluated by the percentage conversion of N_2O and CH_4 to N_2 and CO_2, respectively. The data in the catalytic activity measurements were recorded when the reaction reached steady state after 30 min.

3. Results and discussion

3.1. Reduction of N_2O by CH_4 in the absence of O_2 ($N_2O + CH_4$ system)

Figure 1 (a) and (b) shows the dependence of the composition of CH_4 (0–500 ppm) for the N_2O conversion into

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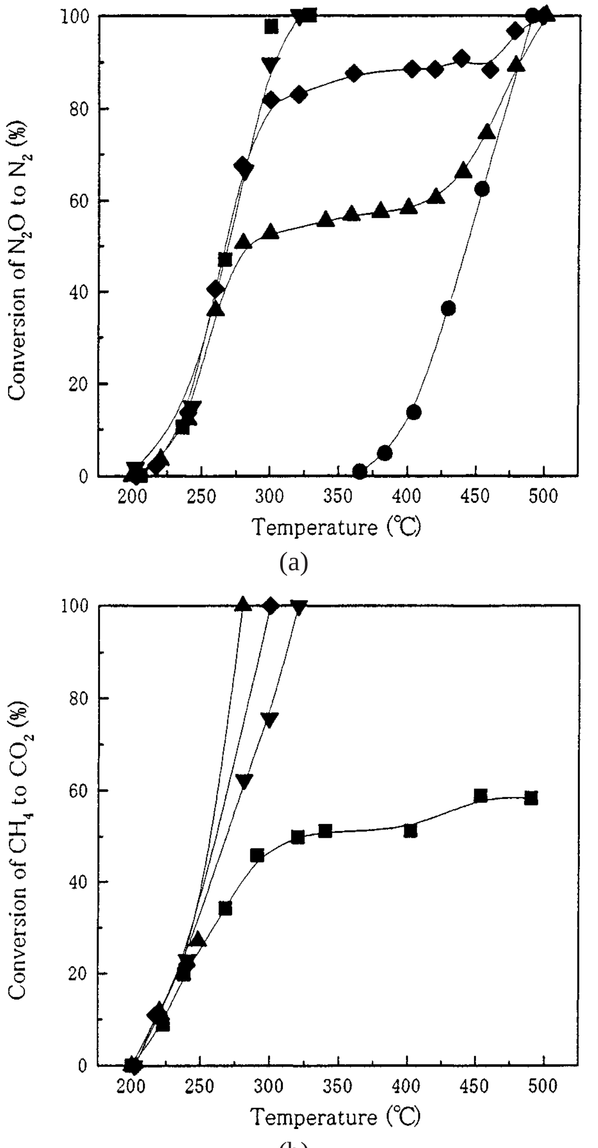
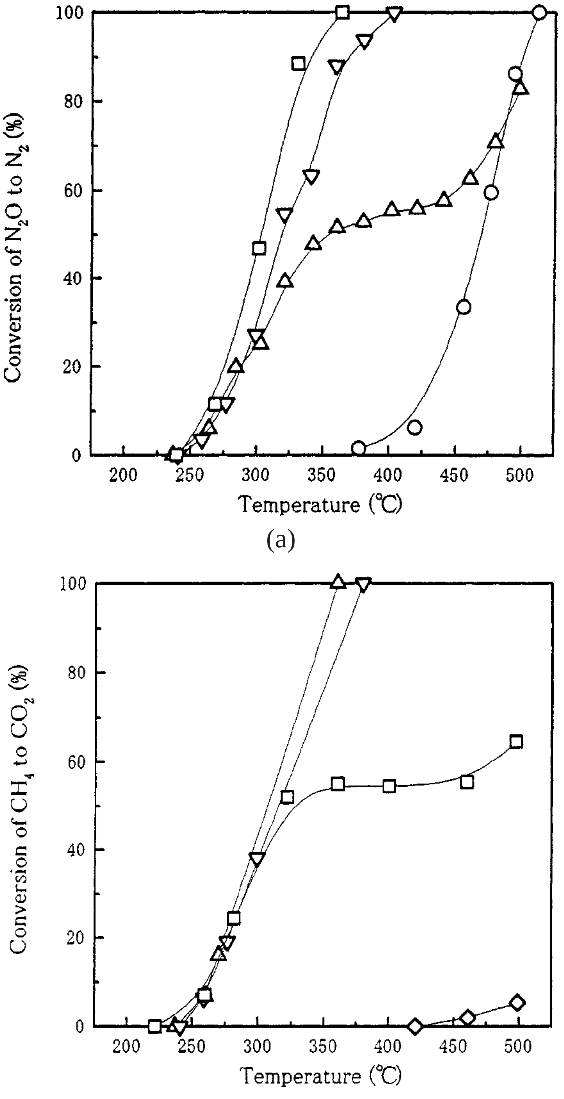


(a)

(b)

Figure 1. Reaction of N_2O with CH_4 in the $N_2O + CH_4$ mixture: the conversion of (a) N_2O into N_2 and (b) of CH_4 into CO_2. (●) N_2O (950 ppm), (▲) N_2O (950 ppm) + CH_4 (130 ppm), (◆) N_2O (950 ppm) + CH_4 (200 ppm), (▼) N_2O (950 ppm) + CH_4 (240 ppm) and (■) N_2O (950 ppm) + CH_4 (500 ppm).



(a)

(b)

Figure 2. Reaction of N_2O with CH_4 in the $N_2O + CH_4 + O_2$ mixture: the conversion of (a) N_2O into N_2 and (b) of CH_4 into CO_2. (○) N_2O (950 ppm) + O_2 (10%), (△) N_2O (950 ppm) + CH_4 (130 ppm) + O_2 (10%), (▽) N_2O (950 ppm) + CH_4 (240 ppm) + O_2 (10%), (□) N_2O (950 ppm) + CH_4 (500 ppm) + O_2 (10%) and (◇) CH_4 (500 ppm) + O_2 (10%).

N_2 and the CH_4 conversion into CO_2, respectively. The catalytic activity of N_2O decomposition on Fe-BEA catalyst was significantly promoted by the presence of CH_4. Increasing of N_2O conversions correlated well with that of CH_4 conversions. As shown in figure 1(a), N_2O conversions were hardly influenced by the composition of CH_4 (130–500 ppm) in the N_2O/CH_4 reaction gas at the low N_2O conversion range (<40%). N_2, H_2O and CO_2 were detected as the products in these catalytic experiments. The plateaus in the N_2O conversion curves (in 130 and 200 ppm CH_4) and the CH_4 conversion curve (in 500 ppm CH_4) were observed after the CH_4 conversion or the N_2O conversion reached at 100% (figure 1). This is due to the fact that CH_4 or N_2O in the mixture gas was completely consumed by the reaction with N_2O or CH_4 at these temperatures. The result suggests that N_2O reacts with CH_4 to produce N_2, CO_2 and H_2O under the N_2O/CH_4 mixture flow. As shown in figure 1, the stoichiometry between N_2O and CH_4 in this reaction over Fe-BEA zeolite was 4 : 1 (950 ppm N_2O : 240 ppm CH_4). Therefore, the overall reaction is represented by

$$4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O \qquad (1)$$

3.2. Reduction of N_2O by CH_4 in the presence of excess O_2 ($N_2O + CH_4 + O_2$ system)

Figure 2 (a) and (b) shows the dependence of the composition of the N_2O (950 ppm) + CH_4 (0–500 ppm) + O_2

Table 1
Turnover rates and apparent activation energies for various reaction systems over Fe-BEA.

Reaction system[a]	Turnover rate ($\times 10^{-4}$ mol s^{-1} Fe-ion^{-1})		Activation energy (kcal mol^{-1})	
	N_2 formation	CO_2 formation	N_2 formation	CO_2 formation
N_2O[b]	16.8	–	44 ± 3	–
$N_2O + CH_4$[c]	25.7	4.8	21 ± 1	24 ± 1
$N_2O + O_2$[b]	7.8	–	49 ± 3	–
$N_2O + CH_4 + O_2$[c]	9.2	2.3	23 ± 1	25 ± 1
$CH_4 + O_2$[d]	–	1.4	–	52 ± 4

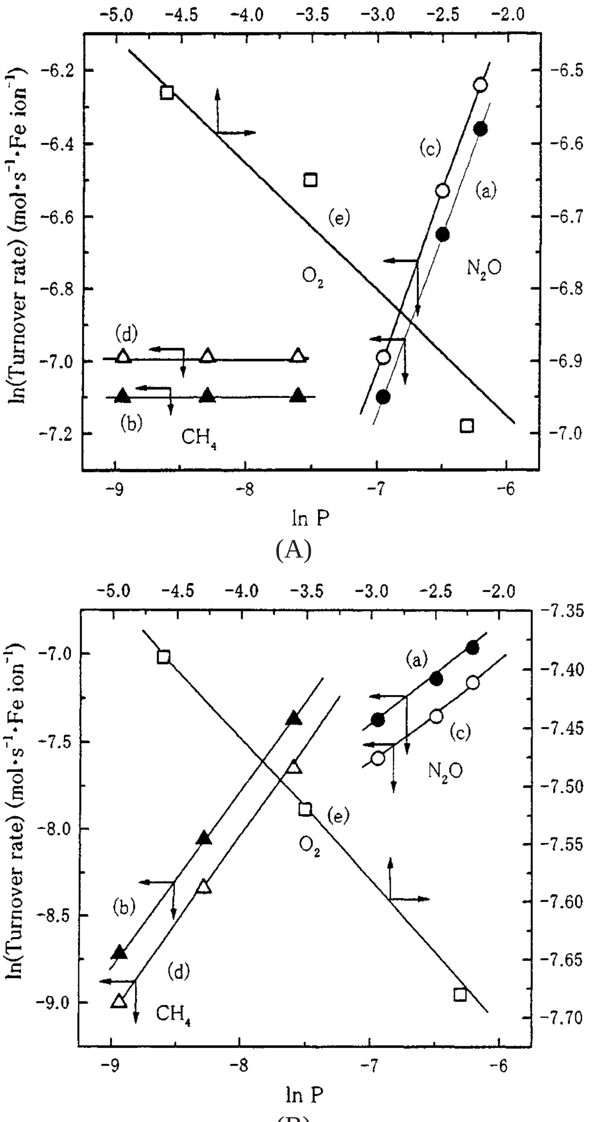
[a] The composition of the reactants: N_2O (950 ppm), CH_4 (240 or 500 ppm) and O_2 (10%) in He balance.
[b] Reaction ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$) at 430 °C.
[c] Reaction ($N_2O + \frac{1}{4}CH_4 \rightarrow N_2 + \frac{1}{4}CO_2 + \frac{1}{2}H_2O$) in 240 ppm CH_4 at 275 °C.
[d] Reaction ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$) in 500 ppm CH_4 at 500 °C.

(10%) reaction system for the N_2O conversion into N_2 and the CH_4 conversion into CO_2, respectively. Although the catalytic activities of the direct decomposition of N_2O and the reduction of N_2O by CH_4 were inhibited slightly by the presence of O_2, the same catalytic behavior of N_2O reduction by CH_4 as in figure 1 was observed in these experimental conditions (promoting effect by CH_4). As shown in figure 2, the N_2O conversion was influenced by the concentration of CH_4 (in 130–500 ppm CH_4). However, the N_2O conversion hardly depended on the concentration range above 500 ppm CH_4, since the same N_2O conversion curve as in the 500 ppm CH_4 was obtained even at 3000 ppm CH_4 [3]. It is interesting that the same behavior of the plateaus in the CH_4 conversion curve (in 500 ppm CH_4) and the N_2O conversion curve (in 130 ppm CH_4) as in figure 1 were observed even in the presence of excess O_2 after the N_2O or CH_4 conversion (ca. 350–450 °C) reached at 100% (figure 2). The same products (i.e., N_2, CO_2 and H_2O) as in the $N_2O + CH_4$ reaction were observed in these experiments. It should be noted that the oxidation of CH_4 by O_2 over the Fe-BEA catalyst began above 450 °C (figure 2(b)). These results indicate that the reduction of N_2O by CH_4 and the oxidation of CH_4 by N_2O are scarcely influenced by the presence of O_2 (10%). Moreover, these reactions took place at much lower temperatures (250–350 °C) than each of the original reaction temperatures in the direct N_2O decomposition (>400 °C) and the CH_4 oxidation (>450 °C). Previously, Panov et al. [6] reported that an O atom from a N_2O molecule, which cannot be produced by O_2, readily reacted with CH_4 to produce CH_3OH over a Fe/ZSM5 catalyst even at room temperature. This finding implies that the O atom from the N_2O molecule is much more active and efficient in activating CH_4 than that from the O_2 molecule. Therefore, it is strongly supported that N_2O reacts selectively with CH_4 to produce N_2, CO_2 and H_2O at the low temperatures (<400 °C) even in the presence of excess O_2. In the case of the presence of O_2, the stoichiometry between N_2O and CH_4 was also 4 : 1 (950 ppm N_2O : 240 ppm CH_4). The overall stoichiometry of this reaction could be represented by the same formula as in the case of the absence of O_2 (equation (1)).

3.3. Kinetic studies

In order to understand in more detail the SCR of N_2O with CH_4 over Fe-BEA zeolite, we examined the kinetic parameters of this reaction. Turnover rates (mol s^{-1} Fe-ion^{-1}) of N_2 and CO_2 formation, which were based on figures 1 and 2, were estimated by assuming that all of loaded Fe (exchanged with Fe^{2+}) play as active sites. The apparent activation energies and the typical turnover rates of N_2 formation and CO_2 formation are given in table 1. The activation energy of N_2 formation for the direct decomposition of N_2O (N_2O alone) was almost similar to that of N_2O in the presence of O_2 ($N_2O + O_2$). The activation energy of N_2 formation for the reduction of N_2O by CH_4 was much lower than that for the direct decomposition of N_2O (in the $N_2O + CH_4$ and $N_2O + CH_4 + O_2$ systems). Reduction of N_2O by CH_4 (in N_2 formation) and oxidation of CH_4 by N_2O (in CO_2 formation) also proceeded with almost the same activation energies. Moreover, these activation energies hardly depended on the presence of O_2. The activation energy of CO_2 formation for the oxidation of CH_4 by O_2 was much higher than that for the oxidation of CH_4 by N_2O in both the $N_2O + CH_4$ and the $N_2O + CH_4 + O_2$ system. These results support that the reduction of N_2O by CH_4 and the oxidation of CH_4 by N_2O in the reaction between N_2O and CH_4 concomitantly occur whether in the presence of O_2 or not.

Figure 3 shows ln–ln plots of the turnover rates of N_2 formation and CO_2 formation against the partial pressure of N_2O, CH_4 and O_2 in the N_2O/CH_4 and $N_2O/CH_4/O_2$ reactions. Kinetic orders with respect to N_2O, CH_4 and O_2 were determined by following the turnover rates of formation of N_2 and CO_2. It should be noted that the turnover rates were calculated based on the conversions of reactants (N_2O and CH_4) in the range between 5 and 20%. As shown in figure 3, good linear correlations in the ln–ln plots were obtained with these experimental conditions. The empirical reaction orders are given in table 2, which was estimated from figure 3. The turnover rates of N_2 formation were found to be first order with respect to N_2O, and zero order with respect to CH_4 whether in the presence of O_2 or not. The turnover rates of CO_2 formation were 0.6 order with respect to N_2O, and first order with respect to CH_4



(A)

(B)

Figure 3. Dependence of the turnover rates of (A) N_2 formation and (B) of CO_2 formation in the $N_2O + CH_4$ and $N_2O + CH_4 + O_2$ mixture systems on the partial pressures of the reactants. The composition of reaction mixture: (a) N_2O (950, 1500 and 2000 ppm) + CH_4 (500 ppm), (b) N_2O (950 ppm) + CH_4 (130, 240 and 500 ppm), (c) N_2O (950, 1500 and 2000 ppm) + CH_4 (500 ppm) + O_2 (10%), (d) N_2O (950 ppm) + CH_4 (130, 240 and 500 ppm) + O_2 (10%) and (e) N_2O (950 ppm) + CH_4 (500 ppm) + O_2 (1, 3 and 10%).

whether in the presence of O_2 or not. Both the turnover rates of N_2 formation and of CO_2 formation were slightly negative order with respect to O_2. The difference in the reaction order with respect to CH_4 between N_2 formation (zero order) and CO_2 formation (first order) may reflect substantially the difference in the reaction pathways between the N_2O decomposition and the CH_4 oxidation (in the SCR of N_2O by CH_4). In general, N_2 formation from N_2O decomposition is attained by simply the dissociation of a N–O bond over catalyst surface, while CO_2 formation from CH_4 oxidation requires several steps, e.g., dissociation of a C–H bond and formation of a C–O bond. It has been reported in the literature that the reaction rate of the N_2O decomposition is first order in N_2O and -0.5 order in O_2 [2,7]. The reaction rate of the CH_4 oxidation over noble metal catalysts is well known to be first order in CH_4 and zero order in O_2 [8–10]. The empirical reaction orders in table 2 (positive orders with respect to N_2O for both N_2 and CO_2 formation and first order with respect to CH_4 for CO_2 formation) show that the reaction rate of the CO_2 formation during the SCR of N_2O by CH_4 is determined by both the formation of an O atom from N_2O and the activated adsorption of CH_4 over the Fe-BEA catalyst, while the reaction rate of the N_2 formation is determined by only the activation of N_2O. Although the reaction order for the N_2 formation with respect to CH_4 is zero, CH_4 plays an important role in the N_2O reduction (i.e., formation of active sites on the Fe-BEA surface), because the catalytic activities in N_2O conversion were drastically enhanced by the presence of CH_4 (figures 1(a) and 2(a)). It is also indicated that O_2 during the SCR of N_2O by CH_4 acts to some extent as inhibiting species on the active sites for both N_2 and CO_2 formation. We are currently undertaking further investigation in our laboratory with respect to the detailed mechanism in the SCR of N_2O with hydrocarbons (e.g., CH_4, C_2H_6, C_3H_6, etc.) on Fe-zeolite catalysts [11].

4. Conclusion

The present study has demonstrated that simultaneous removal of N_2O and CH_4 as the strong greenhouse-effect gases is effectively performed by the SCR of N_2O with CH_4 over a Fe-BEA catalyst even in the presence of excess O_2. The kinetics parameters are the same whether O_2 is present or not, and the reaction between N_2O and CH_4 occurs selectively. The overall stoichiometry of this reaction is represented by $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$.

Table 2
Empirical reaction orders.

Reaction system	Reaction order in N_2 formation			Reaction order in CO_2 formation		
	N_2O	CH_4	O_2	N_2O	CH_4	O_2
$N_2O + CH_4$[a]	1.0	0	–	0.6	1.0	–
$N_2O + CH_4 + O_2$[b]	1.0	0	-0.2	0.6	1.0	-0.1

[a] Reaction orders at 240 °C.
[b] Reaction orders at 275 °C.

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