Isotopic study of N_2O decomposition on an ion-exchanged Fe-zeolite catalyst: mechanism of O_2 formation

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N_2O decomposition on an ion-exchanged Fe-MFI catalyst has been studied using an ^{18}O-tracer technique in order to reveal the reaction mechanism. $N_2{}^{16}O$ was pulsed onto an $^{18}O_2$-treated Fe-MFI catalyst at 693 K, and the O_2 molecules produced were monitored by means of mass spectrometry. The ^{18}O fraction in the produced oxygen had almost half the value of that on the surface oxygen, and $^{18}O^{18}O$ was not detected. The result shows that O_2 formation proceeds *via* the Eley–Rideal mechanism ($N_2{}^{16}O + {}^{18}O(a) \rightarrow N_2 + {}^{16}O^{18}O$).

KEY WORDS: ^{18}O isotope; Fe-MFI catalyst; N_2O decomposition; reaction mechanism.

1. Introduction

Nitrous oxide (N_2O) is a strong greenhouse-effect gas with a global warming potential (GWP) per molecule of about 300 times that of carbon dioxide (CO_2), and it also takes part in the destruction of the stratospheric ozone layer [1]. From the point of view of the environment, therefore, the catalytic decomposition of N_2O ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$) has been attracting much attention [1–15]. Various research groups have studied metal oxides (including mixed oxides) [2–5], supported noble metals (Rh, Ru) [6–10] and transition metal exchanged zeolites (Cu-MFI, Fe-FAU, etc.) [11–13] for N_2O decomposition at different temperatures (500–800 K).

For metal oxides and/or mixed oxide system [4,5], the mechanism of N_2O decomposition has been discussed in terms of the Langmuir–Hinshelwood (LH) mechanism (steps (1) and (2)):

$$N_2O \rightarrow N_2 + O(a) \qquad (1)$$

$$2O(a) \rightarrow O_2 \qquad (2)$$

$$N_2O + O(a) \rightarrow N_2 + O_2. \qquad (3)$$

Step (1) is the dissociative N_2O adsorption followed by the production of N_2 and adsorbed oxygen on the catalyst surface. Step (2) is the O_2 formation by the recombinative desorption of adsorbed oxygen, which may occur at relatively higher temperatures (>650 K). As a mechanism of O_2 formation, however, the Eley–Rideal (ER) mechanism (step (3)) has also been proposed [13–15]. Step (3) is the oxygen removal by a direct collision of N_2O with adsorbed oxygen, which might be possible at relatively lower temperatures. Steps (1) and (3) correspond to the so-called redox process [13,15]. Dandl and Emig [14] proposed a mechanistic model from the kinetics simulation, where the ER mechanism prevails at lower temperatures and the LH mechanism prevails at higher temperatures.

We have reported that an Rh/USY catalyst was very active for the catalytic decomposition of N_2O even at low temperatures around 500 K [7,8]. The O_2 production started on an oxygen-covered Rh surface at low temperatures, but the O_2-TPD measurement in an He flow showed that O_2 was not desorbed up to 900 K [16]. To elucidate the mechanism of O_2 formation, we have established an isotopic tracer method, where $N_2{}^{16}O$ is pulsed onto an $^{18}O_2$-treated catalyst surface [16,17]. Surprisingly, the O_2 formation was found to proceed *via* the LH mechanism (step (2)) over oxidized Rh black and supported Rh (Rh/USY, Rh/SiO_2) catalysts at 493 K [16–18]. Because the recombinative desorption of oxygen did not occur in He at 493 K (the O_2-TPD [16]), we have proposed reaction-assisted desorption of O_2 during N_2O decomposition at low temperature [16,17].

For ion-exchanged Fe-zeolite catalysts (Fe-FAU, Fe-MOR), the catalytic decomposition rate of N_2O is first-order in N_2O, but a near-zero-order in O_2, which suggests that the ER mechanism prevails [13,15]. To confirm the mechanism of O_2 formation, Leglise *et al.* [13] conducted an ^{18}O-tracer experiment using $N_2{}^{16}O$ in a recirculation system, but the tracer data did not conform to the expectation from the kinetic data. In fact, the first dioxygen molecules observed were virtually all $^{16}O^{16}O$, and Leglise *et al.* [13] suggested that only a very small fraction of the exchanged Fe cations are active, but that otherwise the decomposition reaction is unrelated to the redox process (the ER mechanism). Further experiments using $N_2{}^{18}O$ on an Fe-MOR

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catalyst also failed to conform to the expectation, because the reaction mechanism was disguised by the exchange of $N_2{}^{18}O$ with the catalyst oxygen [19].

In this work, our ^{18}O tracer technique [16,17] was applied to an ion-exchanged Fe-zeolite (Fe-MFI) catalyst to elucidate the mechanism of N_2O decomposition. This paper presents direct evidence of the ER mechanism for O_2 formation (step (3)).

2. Experimental

An Fe-MFI ($SiO_2/Al_2O_3 = 23.8$) catalyst was prepared by ion-exchange with a dilute solution of $FeSO_4$ at 323 K for 20 h under a nitrogen atmosphere, followed by calcination in air at 773 K for 12 h [20,21]. The zeolite support (Na-MFI, $SiO_2/Al_2O_3 = 23.8$) was supplied by Tosoh Co. The loading weight of Fe on MFI support was 2.9 wt% (80% exchanged with Fe^{2+}). The O_2-TPD experiment was carried out in a microcatalytic pulse reactor in order to study at what temperatures O_2 is desorbed from the catalyst [16]. The He carrier flow rate was 55 cm^3/min. The temperature was increased from room temperature to 1073 K at a constant heating rate of 10 K/min and was kept at 1073 K.

The reaction of N_2O decomposition on an $^{18}O_2$-treated Fe-MFI catalyst was performed in the same reactor as for the O_2-TPD study. A quartz tube reactor (8 mm i.d.) was charged with 50.2 mg of the Fe-MFI catalyst (4 mm in height, Fe = 26.1 μmol). Highly purified He (99.9999%) was used as a carrier gas at a flow rate of 55 cm^3/min. Isotope-labeled $^{18}O_2$ (96.5% $^{18}O_2$) was obtained from Icon Company Ltd. The ^{18}O tracer-loaded catalyst was prepared as follows: the catalyst was treated with $^{18}O_2$ (110 Torr) three times in an *in situ* closed system at 773 K for 1 h after H_2 reduction at 773 K. The reactant gas (0.50% $N_2{}^{16}O$ in He) and probe gases (0.22% $^{18}O_2$ in He and 0.32% $C^{16}O_2$ in He) were flushed onto the catalyst *via* the carrier gas. The amount of N_2O was 0.38 μmol/pulse, $^{18}O_2$—0.17 μmol/pulse, and CO_2—0.11 μmol/pulse. The effluent was analyzed in an on-line gas chromatograph (Shimadzu, GC-8A) equipped with Molecular Sieve 5 Å and Porapak Q and differentially pumped quadrupole mass spectrometer (Balzers, QMS 200 F). To prevent leakage of $^{16}O_2$ from the atmosphere into the gas line, the whole apparatus, which was located in a corner of the laboratory room, was isolated from the atmosphere by drawing curtains to make a small room in which N_2 gas was purged [16].

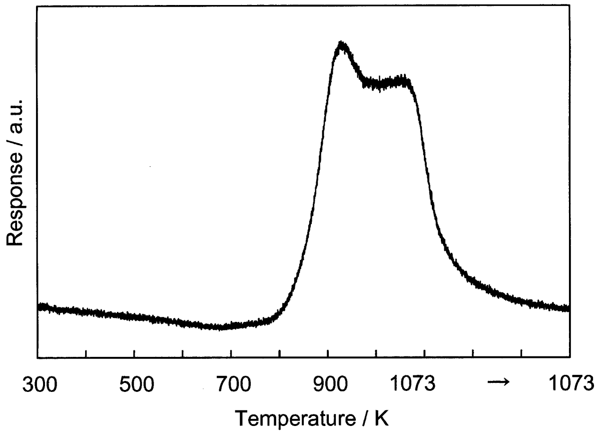

Figure 1. O_2-TPD profile from Fe-MFI catalyst after O_2 treatment at 773 K for 1 h.

3. Results and discussion

The N_2O decomposition reaction on the Fe-MFI catalyst after O_2 treatment at 773 K was carried out using N_2O pulses in a temperature range of 653–753 K. The pulsed N_2O conversion was 12% at 693 K, and reached 100% at 753 K. In the steady-state N_2O decomposition on the same catalyst [22], the N_2/O_2 ratio of the product molecules was 2. In this study, however, the N_2/O_2 ratio was 4, indicating that half the amount of oxygen was adsorbed on the catalyst during the N_2O pulse even after the O_2 treatment at 773 K. It should also be noted that the impregnated Fe/MFI catalyst was inactive for N_2O decomposition [21,22], suggesting that the active species are the ion-exchanged Fe. Figure 1 shows the O_2-TPD spectrum over the Fe-MFI catalyst pretreated in O_2 at 773 K for 1 h. O_2 desorption started above 770 K with a maximum occurring around 930 K. No O_2 peak was observed at the temperatures below 770 K. The O/Fe ratio was 0.17. Voskoboinikov *et al.* [23] reported that the O/Fe ratio depends significantly on the SiO_2/Al_2O_3 ratio. Our result (O/Fe = 0.17) may be reasonable in terms of their data.

Fe-MFI catalyst after H_2 treatment was oxidized with the $^{18}O_2$ gas at 773 K, and pulsed N_2O decomposition was carried out at 693 K. Generally, an isotopic equilibrium constant, K_e, should be considered to judge incidental exchange reactions that would disguise the experimental results. Taking into account an equilibrium reaction,

$$^{18}O_2 + {}^{16}O_2 \Leftrightarrow 2\,{}^{18}O^{16}O, \tag{4}$$

K_e is generally given as

$$K_e = \frac{[^{18}O^{16}O]^2}{[^{18}O_2][^{16}O_2]}. \tag{5}$$

If the exchange reaction equilibrates, K_e should be close to 4 [24]. The same rule applies for other exchange reactions. An isotopic fraction of ^{18}O [$^{18}f = {}^{18}O/({}^{16}O + {}^{18}O)$] on the catalyst can be evaluated by a pulsed $C^{16}O_2$ experiment. It should be noted that the amount of the CO_2 pulse (0.11 μmol) is negligible compared with that of the ion-exchanged Fe atoms (26.1 μmol). Table 1 shows the ^{18}f and K_e in the product

Table 1
The isotopic fraction of ^{18}O (^{18}f) and the isotopic equilibrium constant (K_e) in the product molecules from $^{18}O_2$, $C^{16}O_2$ and $N_2{}^{16}O$ pulses at 693 K.

Experiment No.	Pulse	Surface species	Product	$^{18}f_{obs.}$	K_e
1	$C^{16}O_2$	^{18}O	CO_2	0.23	3.95
2	$N_2{}^{16}O$	^{18}O	O_2	0.13	∞
2	$N_2{}^{16}O$	^{18}O	N_2O	0.00 [a]	–
3	$^{18}O_2$	^{16}O	O_2	0.95	0.18
4	$^{18}O_2$	–	O_2	0.97 [b]	–

[a] The isotopic abundance of ^{18}O is 0.002.
[b] The ^{18}f in the incident pulse measured without the catalyst.

molecules obtained at 693 K. The exchange reaction of oxygen in CO_2 is fast on metal oxides [24]. As shown in table 1 (experiment 1), K_e is 3.95, which suggests that the isotopic exchange of oxygen in CO_2 equilibrates. Therefore, the ^{18}f in the product CO_2 should be equal to that of the surface oxygen. Since the ^{18}f in the product CO_2 was 0.23 (table 1, experiment 1), the ^{18}f on the Fe-MFI catalyst after the $^{18}O_2$ treatment was determined to be 0.23. As a separate experiment, the $^{18}O_2$ pulse was injected onto $^{16}O_2$-treated catalyst at 693 K (table 1, experiment 3). Comparing the ^{18}f value measured without the catalyst (0.97; table 1, experiment 4) with 0.95, the exchange coefficient of O_2 (b_0) with the surface oxygen (step (6)) was estimated to be 0.02:

$$^{18}O_2 + {}^{16}O(a) \rightarrow {}^{18}O^{16}O + {}^{18}O(a). \qquad (6)$$

The exchange coefficient represents the isotope fraction produced during a single pass of O_2 exchanging with the surface oxygen. It should be noted that the b_0 value was much lower than those of the Rh catalysts [16,17].

After the pulsed CO_2 experiment, an $N_2{}^{16}O$ pulse was injected onto the $^{18}O_2$-treated catalyst at 693 K (table 1, experiment 2). The ^{18}f of the product O_2 was 0.13, which was almost half the value of ^{18}f on the catalyst. In addition, the K_e value of oxygen produced from N_2O decomposition was infinity (table 1, experiment 2), because $^{18}O_2$ was not detected. As the K_e value was far from 4, the product O_2 was not in equilibrium. Furthermore, the exchange reaction of oxygen in N_2O with the surface oxygen (step (7)) can be neglected because of the very low ^{18}f value in the outlet N_2O (table 1, experiment 2):

$$N_2{}^{16}O + {}^{18}O(a) \rightarrow N_2{}^{18}O + {}^{16}O(a). \qquad (7)$$

In the case of the Rh catalysts [16,17], all of the surface oxygen was involved in the recombinative desorption of O_2 (the LH mechanism: step (2)). If this is the case, the ^{18}f of the product oxygen should be the same as that on the surface oxygen (*i.e.*, 0.23). The observed ^{18}f value (0.13) is quite different from 0.23. If nascent O(a) atoms produced only from $N_2{}^{16}O$ (step (1)) are desorbed *via* step (2), ^{18}f of the product O_2 should be zero, which is again quite different from the observed value (0.13). Therefore, the recombinative desorption of O(a) (step (2)) can be excluded.

In the case of the ER mechanism (*i.e.*, step (3)), the ^{18}O fraction of the product O_2 should be half the value of that on the surface oxygen. After considering the exchange coefficient ($b_0 = 0.02$), the corrected ^{18}f value of the product oxygen is 0.12, which is similar to the observed ^{18}f value. In addition, $^{18}O_2$ was not produced ($K_e = \infty$) from N_2O decomposition. These experimental results strongly support the ER mechanism (*i.e.*, $N_2{}^{16}O + {}^{18}O(a) \rightarrow N_2 + {}^{16}O^{18}O$).

The present result is in contrast to the mechanism of N_2O decomposition over supported Rh catalysts [16,18], where LH-type desorption has been proposed. For some systems such as ion-exchanged Fe-zeolite catalysts, where active sites are isolated, it may be reasonable that the ER mechanism prevails [25]. The active sites of N_2O decomposition over Fe-MFI catalyst may be Fe ion species such as binuclear Fe-oxo species [26–28]. On the other hand, Delahay *et al.* [29] proposed that mononuclear Fe-oxo species are the most active sites for SCR of N_2O with NH_3. The isotopic study in this work clearly showed that O_2 is formed *via* step (3) (*i.e.*, the ER mechanism) when $N_2{}^{16}O$ was pulsed on the $^{18}O_2$-treated Fe-MFI catalyst. The ER mechanism may also prevail during a steady-state N_2O decomposition reaction, although further work is needed in various Fe-zeolite systems.

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