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Mechanism of N_2O decomposition over a Rh black catalyst studied by a tracer method

The reaction of N_2O with $^{18}O(a)$

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Abstract

N_2O decomposition on an unsupported Rh catalyst has been studied using tracer technique in order to reveal the reaction mechanism. $N_2{}^{16}O$ was pulsed onto ^{18}O/oxidized Rh catalyst at 220°C and desorbed O_2 molecules ($m/e = 32, 34, 36$) were monitored by means of mass spectrometer. The ^{18}O fraction in the desorbed dioxygen was the same value as that on the surface oxygen. The result shows that the O_2 molecules desorb via Langmuir–Hinshelwood mechanism, i.e., the desorption of dioxygen through the recombination of adsorbed oxygen. On the other hand, TPD measurements in He showed that desorption of oxygen from the Rh black catalyst occurred at the higher temperatures. Therefore, reaction-assisted desorption of oxygen during N_2O decomposition reaction at the low temperature was proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: ^{18}O isotope; N_2O decomposition; A Rh black catalyst; Reaction mechanism

1. Introduction

Recently, the catalytic decomposition of N_2O, a strong green-house effect gas, has been attracting much attention [1], and Rh catalysts such as Rh/ZSM-5 [2] and Rh/ZnO [3] were found to have high activities at low reaction temperatures (250–350°C). In particular, we have shown that the steady-state decomposition reaction ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$) takes place on Rh/USY catalysts, etc., even at the low temperatures around 250°C [4,5]. On the other hand, temperature-programmed desorption (TPD) experiments show that oxygen molecules desorb from Rh surfaces at much higher temperatures over 600°C [5,6]. Therefore, it is an open question why O_2 is desorbed at such low temperatures during the catalytic N_2O decomposition over the Rh catalysts.

The mechanisms of N_2O decomposition have been given as follows [1,7]:

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

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

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

Step (1) shows the dissociative N_2O adsorption followed by the production of N_2 and adsorbed oxygen on the catalyst surface. Step (2) shows the oxygen removal by the recombinative desorption of oxygen, and so-called Langmuir–Hinshelwood (LH) mechanism is described by steps (1) and (2). As stated above,

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however, it may be difficult to understand that the step (2) prevails at the low temperatures. Step (3) shows the oxygen removal via Eley–Rideal (ER) mechanism [8], which might be possible at relatively low reaction temperatures [9]. Dandl and Emig [9] proposed a mechanistic model from the kinetics simulation, where ER mechanism prevails at lower temperatures and LH mechanism prevails at higher temperatures. Hot-atom (HA) mechanism [10] may also be considered, where only hot (nascent) O(a) atoms produced by the step (1) are desorbed via the step (2).

Isotope tracer studies using ^{18}O will be useful to elucidate the mechanism of the oxygen removal. Leglise et al. [8] studied the N_2O decomposition over ^{18}O covered Fe/mordenite catalysts at a temperature range 350–700°C. However, the reaction mechanism was disguised by the diffusion of oxygen from the zeolite support. In this work, we used an unsupported Rh catalyst (i.e., Rh black catalyst), and to make clear the reaction mechanism the ^{18}O tracer technique was applied using the unsupported Rh catalyst in a pulse reaction system. TPD of O_2 in He from the Rh black catalyst was also studied. Surprisingly, the reaction was found to proceed via LH mechanism in spite of low temperature like 220°C.

2. Experimental

The Rh black catalyst used in this work was prepared by calcinaiton of $Rh(OH)_3$ in oxygen at 300°C for 3 h, which was obtained by adding a slight excess of a sodium hydroxide solution (pH = 7.5–7.8) to a hot aqueous solution (90–95°C) of $RhCl_3{\cdot}3H_2O$ [11]. Hydrogen pretreatment was not carried out because the activity of the catalyst for N_2O decomposition decreased drastically. As will be shown later in TPD measurements, the atomic O/Rh ratio (the ratio of the total number of O atoms to the total number of Rh atoms in the catalyst) was determined to be 1.24 after the O_2 treatment at 300°C. The result shows that the Rh black catalyst was oxidized to RhO_x ($x = 1.24$) by the O_2 treatment.

Pulse experiments were performed in a micro-catalytic pulse reactor [5]. A quartz tube reactor (ID, 4 mm) was charged with 11.6 mg of the catalyst (~2 mm in height, 94.5 μmol as Rh). High-purified He (99.9999%) was used as a carrier gas at a flow rate of 55 cm^3/min. Isotope labeled $^{18}O_2$ (0.20 vol.%, $^{18}O_2$ and 99.8 vol.%, He) was obtained from Isotec, Matheson. The reactant gas (0.516% $N_2{}^{16}O$ in He) and probe gasses ($^{16}O_2$, $^{18}O_2$ and $C^{16}O$) were flushed onto the catalyst via the carrier gas. The amount of N_2O, $^{16}O_2$, $^{18}O_2$ and CO was 0.27, 0.10, 0.10 and 0.04 μmol/pulse, respectively. The effluent was analyzed by on-line gas chromatograph system equipped with TCD detector (Shimadzu, GC-8A) and differentially pumped quadruple mass spectrometer (Balzers, QMS 200 F). In order to prevent leak of $^{16}O_2$ in the atmosphere into the gas line, the whole apparatus was isolated from the atmosphere by drawing curtains in which N_2 gas was purged.

Quantitative TPD measurement in He flow was performed using the Rh black catalyst using 4.3 mg of the catalyst (28 μmol as Rh metal). The analysis equipment used was the same as the isotopic tracer study. The temperature was increased from room temperature to 800°C at a constant heating rate of 10°C/min and was kept at 800°C for 40 min.

Pulsed CO (0.994% CO in He) chemisorption measurements at room temperature were carried out using 5.1 mg of the catalyst (33 μmol as Rh metal). The Rh black catalyst was characterized by evaluating the amounts of absorbed oxygen (O(a)) on the Rh surface by CO_2 emission (i.e., step (4)), and the amounts of adsorbed carbon monoxide (CO(a)) to vacancy sites on the Rh surface (i.e., step (5))

$$CO + O(a) \rightarrow CO_2 + \square \tag{4}$$

$$CO + \square \rightarrow CO(a) \tag{5}$$

where □ indicates vacancy sites.

3. Results and discussion

3.1. Isotopic tracer study

Isotopic tracer study was performed on the Rh black catalyst after the O_2 treatment at 300°C. The surface ^{16}O on the catalyst was exchanged by $^{18}O_2$ at 300°C for 3 h (using 0.20% $^{18}O_2$ in He; the flow rate = 5.0 cm^3/min), followed by N_2O decomposition at 220°C. Generally, an isotopic equilibrium constant, K_e, should be considered in order to judge inciden-

Table 1
The isotopic fraction of ^{18}O, $f_{^{18}O}$, and the isotopic equilibrium constant, K_e, in the product molecules from $^{18}O_2$, $C^{16}O$ and $N_2{}^{16}O$ pulses at 220°C

Experiment No.	Pulse	Surface species	Product	$f_{^{18}O}$	K_e
1	$C^{16}O$	^{18}O	CO_2	0.290	3.71
2	$N_2{}^{16}O$	^{18}O	O_2	0.296	1.40
2	$N_2{}^{16}O$	^{18}O	N_2O	0.002[a]	0
3	$^{18}O_2$	^{16}O	O_2	0.783	0.07
4	$^{18}O_2$	–	O_2	0.970[b]	–

[a] The value of 0.002 is the same as the isotopic abundance of ^{18}O.

[b] The $f_{^{18}O}$ in the incident pulse measured without the Rh catalyst.

tal exchange reactions that disguise the experimental results. Taking into account an equilibrium reaction,

$$^{18}O_2 + {}^{16}O_2 \rightleftarrows 2\,{}^{18}O^{16}O \tag{6}$$

the K_e is generally given as the following equation:

$$K_e = \frac{[^{18}O^{16}O]^2}{[^{18}O_2][^{16}O_2]} \tag{7}$$

If the exchange reaction equilibrates, the K_e should be close to four [12]. The same rule applies for other exchange reactions. An isotopic fraction of ^{18}O [$f_{^{18}O} = {}^{18}O/({}^{16}O + {}^{18}O)$] on the catalyst can be evaluated by pulsed $C^{16}O$ experiment. Table 1 shows the $f_{^{18}O}$ and K_e in the product molecules obtained at 220°C. The CO molecules react with the surface oxygen to form CO_2, and CO conversion was 100% in the pulse experiment at 220°C. The $f_{^{18}O}$ in the product CO_2 should be equal to that of surface oxygen. The exchange reaction of oxygen in CO_2 is fast on metal oxides [12]. As shown in Table 1, K_e is 3.71, which suggests that the isotopic exchange of oxygen in CO_2 almost equilibrates (experiment 1). Since the $f_{^{18}O}$ in the product CO_2 was 0.290 (Table 1), the $f_{^{18}O}$ on the catalyst after the $^{18}O_2$ treatment was determined to be 0.290. As a separate experiment, the $^{18}O_2$ pulse was injected onto ^{16}O-covered catalyst (Table 1, experiment 3). Comparing the $f_{^{18}O}$ value measured without the Rh black catalyst (0.970, experiment 4) with 0.783, and the exchange coefficient of O_2 with the surface oxygen (i.e., steps (8) and (8′)) was estimated to be 0.19.

$$^{18}O_2 + {}^{16}O(a) \rightarrow {}^{18}O^{16}O + {}^{18}O(a) \tag{8}$$

$$^{16}O_2 + {}^{18}O(a) \rightarrow {}^{18}O^{16}O + {}^{16}O(a) \tag{8′}$$

After the pulsed CO experiment, $N_2{}^{16}O$ pulse was injected onto the catalyst at 220°C (experiment 2). The N_2O conversion was about 40%, and the $f_{^{18}O}$ in the product O_2 was 0.296, which was almost the same as $f_{^{18}O}$ on the catalyst surface. In addition, the K_e value of oxygen produced from N_2O decomposition was 1.40, which indicates that the exchange reaction of oxygen between gas phase and surface is slow enough at the low reaction temperature (220°C). Furthermore, the exchange reaction of oxygen in the N_2O with surface oxygen (i.e., step (9)) can be neglected because of the very low $f_{^{18}O}$ value in the outlet N_2O (experiment 2).

$$N_2{}^{16}O + {}^{18}O(a) \rightarrow N_2{}^{18}O + {}^{16}O(a) \tag{9}$$

The mechanism of oxygen desorption is determined by the following discussion. The observed $f_{^{18}O}$ of oxygen produced from the N_2O decomposition and the calculated $f_{^{18}O}$ values based on the three mechanisms (LH, ER and HA) are shown in Fig. 1. In the case of LH mechanism ($2O(a) \rightarrow O_2$: i.e., step (2)), the $f_{^{18}O}$ of the product oxygen should be the same as that of the surface oxygen (i.e., 0.290). Even though the incidental exchange reaction between the products O_2 and the O(a) (i.e., steps (8) and (8′)) occurs, the $f_{^{18}O}$ does not change. As shown in Fig. 1, the experimental result is in good agreement with LH mechanism. In the case of ER mechanism (i.e., step (3)), the $f_{^{18}O}$ of the product oxygen should be the half value of the surface oxygen (i.e., 0.145). However, considering the exchange coefficient 0.19, the $f_{^{18}O}$ of the product oxygen becomes 0.173 (Fig. 1), which is still quite different from the ^{18}O fraction on the surface. Therefore, ER mechanism can be excluded. HA mechanism, which produces O_2

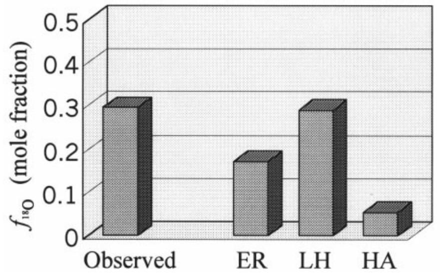

Fig. 1. Comparison of observed and calculated $f_{^{18}O}$ values in desorption of dioxygen during N_2O decomposition.

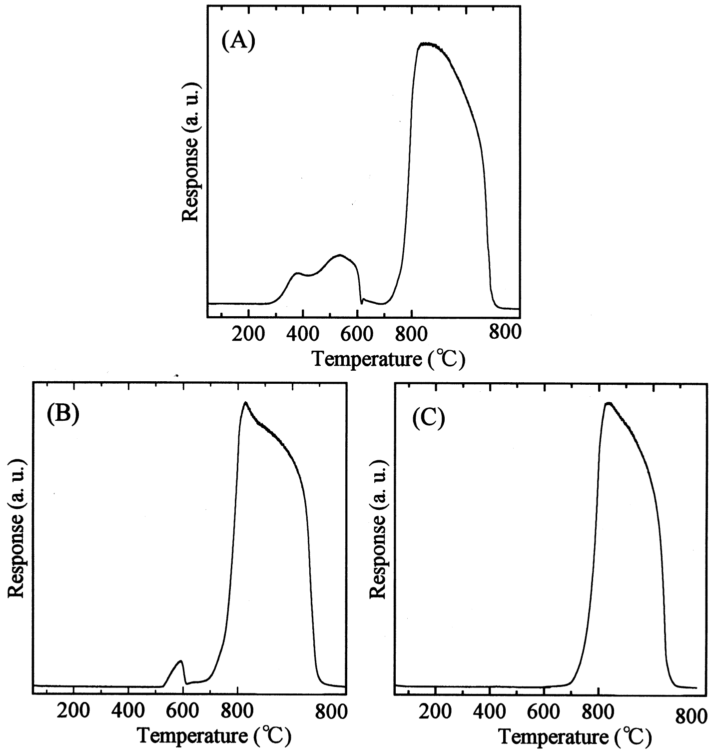

Fig. 2. TPD spectra of O_2 from the Rh black catalysts after the pretreatments: (A), $Rh(OH)_3$ was treated in O_2 at 300°C for 3 h; (B), $Rh(OH)_3$ was treated in He at 300°C for 1 h; (C), the catalyst after the pretreatment (A) was treated in He to 650°C, kept at 650°C for 30 min, and further treated with O_2 at 300°C for 1 h.

molecules only from $N_2{}^{16}O$, can also be excluded. In this case, the $f_{^{18}O}$ is 0.055 (Fig. 1) by only considering step (8′). If the "hot" oxygen can react with all adsorbed oxygen atoms, the $f_{^{18}O}$ becomes the same value as ER mechanism. Therefore, the present result reveals that the oxygen desorption proceeds via LH mechanism.

3.2. Desorption of oxygen from the Rh black catalysts

An O_2-TPD study (in He) showed that O_2 desorption from a supported Rh catalyst was not observed up to 600°C [5]. As shown in the Section 3.1, however, the desorption of O_2 from the Rh black catalyst was observed during the N_2O decomposition at 220°C. The result indicates the difference in the process of O_2 desorption between in the N_2O decomposition and in the thermal desorption. Therefore, in order to elucidate the difference in O_2 desorption, the desorption of oxygen from the Rh black catalyst was examined by O_2-TPD.

Fig. 2(A) shows the O_2-TPD spectrum from the Rh black catalyst after the O_2 treatment at 300°C, which was the same as used in the isotope study (designated by pretreatment (A)). From the total amount of O_2 desorbed, the atomic O/Rh ratio in the catalyst was determined to be 1.24. Most of oxygen ($O/Rh = 1.05$) was desorbed above 700°C, but small O_2 peaks ($O/Rh = 0.19$) were also observed at the temperature range between 300 and 600°C. However, it is clear that the desorption of O_2 did not take place below 300°C. For a comparison, the Rh black catalyst was varied with other pretreatments: $Rh(OH)_3$ was treated in He at 300°C (designated by pretreatment (B)); and the catalyst after the pretreatment (A) was treated in He at 650°C, and further treated with

Table 2
Comparison of O(a)/Rh, CO(a)/Rh and the specific activity of Rh black catalysts after the pretreatments

Pretreatment	O(a)/Rh ($\times 10^{-2}$)[a]	CO(a)/Rh ($\times 10^{-2}$)[b]	Activity ($\times 10^{-2}$ mol site^{-1} s^{-1})[c]
(A)	2.46	2.78	4.25
(B)	2.69	2.95	1.37
(C)	0.06	0.16	3.11

[a] The ratio of the number of adsorbed oxygen atoms to the total number of Rh atoms in the catalyst.

[b] The ratio of the number of adsorbed CO molecules to the total number of Rh atoms in the catalyst.

[c] At 220°C, based on the CO(a)/Rh.

O_2 at 300°C (designated by pretreatment (C)). As shown in Fig. 2(B), only a trace of the O_2 desorption peak at 595°C was observed in the case of the pretreatment (B). The result suggests that most of the O_2 peaks between 300 and 600°C are ascribed to oxygen species which were produced by the oxidation of $Rh(OH)_3$ at 300°C. Fig. 2(C) shows the O_2-TPD spectrum from the pretreatment (C). No O_2 peak below 600°C were observed, which means that the oxygen species are not produced by the reoxidation at 300°C after treating the catalyst in He at 650°C.

The catalytic activities of N_2O decomposition at 220°C after the pretreatments (A), (B) and (C) were measured by the pulse reaction technique. The N_2O conversions at 220°C were 40% (A), 13% (B) and 2% (C). Table 2 shows the comparison of O(a)/Rh, CO(a)/Rh and specific activities of N_2O decomposition after each pretreatment. The pretreatments (A) and (B) show nearly similar O(a)/Rh and CO(a)/Rh values, respectively. On the other hand, the pretreatment (C) drastically decreased O(a)/Rh and CO(a)/Rh values because of severely sintering at the high temperature (at 650°C). Although the amounts of sites on the Rh surface are quite different between the pretreatments (A) and (C), the specific activities are in the same order. However, because the specific activity after the pretreatment (A) was significantly higher than that after the pretreatment (B), the oxygen species (O_2 desorption peaks below 600°C) may play an important role in the high catalytic activity.

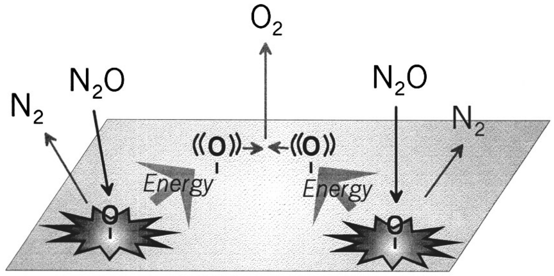

Fig. 3. A proposed model of O_2 desorption during N_2O decomposition.

4. Conclusion

In the present study, the reaction was found to proceed via LH mechanism at 220°C, i.e., all of the surface oxygen on the Rh catalyst are involved in the recombinative desorption of O_2 (i.e., step (2)) at 220°C. The firm conclusion from the TPD study is that desorption of O_2 in He from the catalyst does not take place at 220°C. Therefore, it should be considered that the energy of O–Rh bond formation accompanied by N_2O decomposition may transfer to the surrounding adsorbed oxygen atoms on the catalyst surface, i.e., the O_2 molecules are produced via reaction-assisted desorption. Fig. 3 shows a proposed model of O_2 desorption during N_2O decomposition. In practice, a large bonding energy of O–Rh has been reported (96.8 kcal/mol) [13] and further energy is released by formation of N≡N bond [14]. These exothermic processes can overcome the energy loss caused by the breakage of the NN–O bond. It should also be noted that the overall reaction of N_2O decomposition is exothermic ($\Delta H = -19.5\,\text{kcal/mol}$). We propose the reaction-assisted desorption of oxygen during the N_2O decomposition on the Rh black catalyst. However, more study and discussion will be needed to clarify the dynamics (energy transfer process) of N_2O decomposition and the nature of the active sites for the adsorbed oxygen at low temperature.

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