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Isotopic study of nitrous oxide decomposition on an oxidized Rh catalyst: mechanism of oxygen desorption

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N_2O decomposition on an oxidized Rh catalyst (unsupported) has been studied using a tracer technique in order to reveal the reaction mechanism. $N_2{}^{16}O$ was pulsed onto an ^{18}O/oxidized Rh catalyst at 493 K and desorbed O_2 molecules were monitored. The ^{18}O fraction in the desorbed oxygen had the same value as that on the surface oxygen. The result shows that the oxygen molecules do not desorb via the Eley–Rideal mechanism, but via the Langmuir–Hinshelwood mechanism. On the other hand, desorption of oxygen from Rh surfaces (in vacuum or in He) occurs at higher temperatures, which suggests reaction-assisted desorption of oxygen during the N_2O decomposition reaction at low temperature.

Keywords: ^{18}O isotope, N_2O decomposition, oxidized Rh catalyst, reaction mechanism

1. Introduction

Recently, the catalytic decomposition of N_2O, a strong greenhouse-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 (523–623 K). 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 523 K [4,5]. On the other hand, temperature-programmed desorption (TPD) experiments (in vacuum) show that oxygen molecules desorb from Rh surfaces at much higher temperatures ($\sim$1100 K) [6]. Therefore, it is an open question why O_2 is desorbed at such low temperatures during the catalytic N_2O decomposition over Rh catalysts.

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

$$N_2O \rightarrow N_2 + O_{ad} \tag{1}$$

$$2O_{ad} \rightleftharpoons O_2 \tag{2}$$

$$N_2O + O_{ad} \rightarrow N_2 + O_2 \tag{3}$$

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 the so-called Langmuir–Hinshelwood (LH) mechanism is described by steps (1) and (2). As stated above, however, it may be difficult to understand that step (2) prevails at the low temperatures. Step (3) shows the oxygen removal via the Eley–Rideal (ER) mechanism [7], which might be possible at relatively low reaction temperatures [8]. Dandl and Emig [8] proposed a mechanistic model from the kinetics simulation, where the ER mechanism prevails at lower temperatures and the LH mechanism prevails at higher temperatures. A hot-atom (HA) mechanism [9] may also be considered, where only hot (nascent) O_{ad} atoms produced by step (1) are desorbed via step (2).

Isotope tracer studies using ^{18}O may be useful to elucidate the mechanism of the oxygen removal. Leglise et al. [7] studied the N_2O decomposition over ^{18}O-covered Fe/mordenite catalysts at a temperature range of 623–973 K. However, the reaction mechanism was disguised by the diffusion of oxygen from the zeolite support. In this study, we used an oxidized Rh catalyst without the support and the ^{18}O tracer technique was applied in a pulse reaction system. Temperature-programmed desorption (TPD) of O_2 (in He) from the Rh catalyst was also studied. Surprisingly, the reaction was found to proceed via the LH mechanism at 493 K.

2. Experimental

An unsupported Rh catalyst was prepared by adding a slight excess of a sodium hydroxide solution (pH $=$ 7.5–7.8) to a hot aqueous solution (365 K) of $RhCl_3 \cdot 3H_2O$, followed by calcination in oxygen for 3 h at 573 K [10]. Quantitative TPD measurement (in He flow) was performed in order to study at what temperatures O_2 is desorbed from the catalyst and also to calibrate the oxygen content in the oxidized Rh catalyst. The He 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 for 30 min. As the TPD spectrum will

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be shown later, 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. X-ray diffraction (XRD) measurement indicated that the particles had amorphous structures, but the average particle size of the oxidized Rh was estimated to be about 30 nm from transmission electron microscopy (TEM) observation. These results suggest that the Rh catalyst was not fully oxidized by such a low-temperature oxygen treatment (573 K).

Isotope-labeled $^{18}O_2$ (0.20 vol% $^{18}O_2$ and 99.8 vol% He) was obtained from Isotec Inc., Matheson. A quartz tube reactor (I.D. 4 mm) was charged with 11.6 mg of the catalyst ($\sim$2 mm in height, 94.5 μmol as Rh). Pulse experiments were performed in a micro-catalytic pulse reactor [5]. The catalyst was pretreated in oxygen (30 cm^3/min) at 573 K for 1 h. Hydrogen pretreatment was not carried out because the activity of the catalyst for N_2O decomposition decreased drastically. High-purified helium (99.9999%) was used as the carrier gas at a flow rate of 55 cm^3/min. The reactant gas (0.516% $N_2{}^{16}O$ in helium) and probe gases ($^{16}O_2$, $^{18}O_2$ and $C^{16}O$) were flushed onto the catalyst via the carrier gas. The amount of N_2O was 0.27 μmol/pulse, $^{16}O_2$ as 0.10 μmol/pulse, $^{18}O_2$ as 0.10 μmol/pulse and CO as 0.04 μmol/pulse, respectively.

The effluent was analyzed by an on-line gas chromatograph system equipped with TCD detector (Shimadzu, GC-8A) and differentially pumped quadrupole mass spectrometer (Balzers, QMS 200 F). In order to prevent leakage 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.

3. Results and discussion

The N_2O decomposition reaction on the oxidized Rh catalyst was carried out using N_2O pulses at a temperature range of 473–573 K. The N_2O conversion reached 100% at 573 K. The N_2/O_2 ratio of the product molecules was slightly higher than 2. However, the activity of the decomposition reaction and the N_2/O_2 ratio did not change during 30 pulses of the N_2O injections. This result indicates that the steady decomposition proceeded under the reaction conditions.

The surface ^{16}O on the oxidized Rh catalyst was exchanged by $^{18}O_2$ at 573 K for 3 h (using 0.20% $^{18}O_2$/He; flow rate = 5.0 cm^3/min). Generally, an isotopic equilibrium constant K_e should be considered in order to judge incidental exchange reactions which disguise the experimental results. Taking into account an equilibrium reaction,

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

the K_e is generally given by the following equation:

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

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 493 K.

Experiment No.	Pulse	Surface species	Product	$f_{^{18}O}{}^{a}$	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^b	0
3	$^{18}O_2$	^{16}O	O_2	0.783	0.07
4	$^{18}O_2$	–	O_2	0.970^c	–

[a] The error in the $f_{^{18}O}$ value is ±0.005.
[b] The value of 0.002 is the same as the isotopic abundance of ^{18}O.
[c] The $f_{^{18}O}$ in the incident pulse measured without the Rh catalyst.

If the exchange reaction equilibrates, the K_e should be close to 4 [11]. 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 a pulsed $C^{16}O$ experiment. It should be noted that the amount of the CO pulse (0.04 μmol) is negligible compared with that of surface Rh atoms (ca. 3 μmol), which was estimated from the average particle size. Table 1 shows the $f_{^{18}O}$ and K_e in the product molecules obtained at 493 K. The CO molecules react with the surface oxygen to form CO_2, and CO conversion was 100% in the pulse experiment at 493 K. 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 [11]. 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 surface after the $^{18}O_2$ treatment was determined to be 0.290. As a separate experiment, the $^{18}O_2$ pulse was injected onto the ^{16}O-covered catalyst (table 1, experiment 3). Comparing the $f_{^{18}O}$ value measured without the Rh catalyst (0.970, experiment 4) with 0.783, the exchange coefficient of O_2 (b_{O_2}) with the surface oxygen (steps (6) and (6′)) was estimated to be 0.187. The exchange coefficient means the isotope fraction produced during a single pass of O_2 exchanging with adsorbed oxygen corrected for the background exchange:

$$^{18}O_2 + {}^{16}O_{ad} \rightarrow {}^{18}O^{16}O + {}^{18}O_{ad} \tag{6}$$

$$^{16}O_2 + {}^{18}O_{ad} \rightarrow {}^{18}O^{16}O + {}^{16}O_{ad} \tag{6′}$$

After the pulsed CO experiment, $N_2{}^{16}O$ pulse was injected onto the catalyst at 493 K (experiment 2). The N_2O conversion was $\sim$30%, 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 the gas phase and the surface is slow enough at the low reaction temperature (493 K). Furthermore, the exchange reaction of oxygen in the N_2O with surface oxygen (step (7)) can be neglected because of the very low $f_{^{18}O}$ value in the outlet N_2O (experiment 2):

$$N_2{}^{16}O + {}^{18}O_{ad} \rightarrow N_2{}^{18}O + {}^{16}O_{ad} \tag{7}$$

Table 2
Comparison of observed and calculated $f_{^{18}O}$ values.[a]

	$f_{^{18}O}$
Observed	0.296
LH mechanism	0.290[b]
ER mechanism	0.172
HA mechanism	0.054

[a] The correction for the isotope exchange ($b_{O_2} = 0.187$) is made (see text).

[b] The same value as the ^{18}O fraction on the surface.

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 summarized in table 2. In the case of a LH mechanism ($2O_{ad} \rightarrow O_2$: 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 reactions between the product O_2 and the O_{ad} (i.e., steps (6) and (6′)) occur, the $f_{^{18}O}$ value does not change. The ^{18}O fractions coming from the surface and going to the surface by the exchange reactions are cancelled, because the $f_{^{18}O}$ in the product O_2 is the same as that on the surface in the case of the LH mechanism. As shown in table 2, the experimental result is in good agreement with the LH mechanism. In the case of an ER mechanism (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 ($b_{O_2} = 0.187$), the $f_{^{18}O}$ of the product oxygen becomes 0.172 (table 2), which is still quite different from the ^{18}O fraction on the surface. Therefore, the ER mechanism can be excluded. It should be noted that the product O_2 is formed during contact with the catalyst during N_2O reaction whereas the b_{O_2} value is measured by reaction with just the O_2 pulse. This presumably means that, since oxygen is produced during the reaction, the b_{O_2} value should be corrected for the fact that oxygen is not present in the catalyst bed for the whole time, and presumably be reduced by a factor of 2 (i.e., $b_{O_2} = 0.093$). This leads to the corrected value of $f_{^{18}O}$ for the ER mechanism to be 0.158, which is much more different from the observed $f_{^{18}O}$ value. The HA mechanism, which produces O_2 molecules only from $N_2{}^{16}O$, can also be excluded. In this case, the $f_{^{18}O}$ value is 0.054 (table 2) by only considering step (6′), because the $^{16}O_2$ that is formed can react with adsorbed ^{18}O. If the corrected b_{O_2} value (0.093) is used, the calculated $f_{^{18}O}$ value becomes 0.027, which is quite different from the observed $f_{^{18}O}$ value. If the "hot" oxygen can react with all adsorbed oxygen atoms, the $f_{^{18}O}$ takes the same value as for the ER mechanism. Therefore, the present result reveals that the oxygen desorption proceeds via the LH mechanism (the recombinative desorption of O_2).

The TPD study (in vacuum) showed that oxygen atoms on the Rh(111) surface desorb to form O_2 at ~1100 K [6]. In addition, the TPD experiment (in He) showed that desorption of oxygen from a supported Rh catalyst was not observed up to 873 K [5]. Figure 1 shows the TPD spectrum in the He flow from the unsupported Rh catalyst after the O_2 treatment at 573 K. The small and artificial dip at 894 K was caused by desorption of CO_2. Most of oxygen (the atomic ratio O/Rh = 1.05) was desorbed above 1000 K, but small O_2 peaks (the atomic ratio O/Rh = 0.19) were also observed at the temperature range between 570 and 920 K. It should be noted that the activity of N_2O decomposition was decreased significantly after the catalyst was treated in He at 920 K, and no TPD peak was observed at these temperatures below 920 K after the He treatment followed by O_2 treatment again at 573 K. Therefore, the O_2 peaks at the temperatures below 920 K may play an important role in the high catalytic activity, although it is a subject of future work to elucidate the nature of the active sites including adsorbed oxygen [5]. However, the firm conclusion from figure 1 is that desorption of O_2 (in He) from the catalyst was not observed below 570 K.

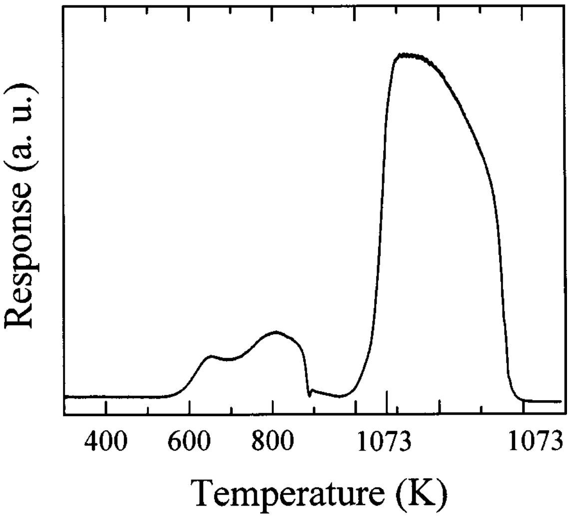

Figure 1. TPD spectrum of O_2 from the oxidized Rh catalyst after calcination in oxygen at 573 K.

In the present study, all of the surface oxygen are involved in the recombinative desorption of O_2 (step (2)) at 493 K. Therefore, it should be considered that a part of the energy of O–Rh bond formation accompanied with 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. In practice, a large bonding energy of O–Rh has been reported (96.8 kcal/mol) [12] and further energy is released by formation of the N≡N bond [13]. 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 ($\Delta H = -19.5$ kcal/mol). We propose the reaction-assisted desorption of oxygen during the N_2O decomposition on the oxidized Rh catalyst. However, more study and discussion will be needed to clarify the dynamics (energy transfer process) of N_2O decomposition in detail.

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