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Investigation on catalysts for the direct decomposition of nitrous oxide for waste anesthetic gas purification

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ABSTRACT

The catalytic reaction of the direct decomposition of nitrous oxide (N_2O) was investigated over Al_2O_3- and SiO_2-supported Pd, Ru, Rh and Pt catalysts as a part of development of catalytic system for purifying waste anesthetic gas. Effects of three gases of O_2, H_2O and isoflurane ($CHF_2OCHClCF_3$) as a representative of halogenated ethers were investigated because they are inevitably present in the waste anesthetic gas. The N_2O decomposition activity of 5 wt% Pd/Al_2O_3 was little affected by coexisting O_2. Coexisting H_2O caused reversibly deterioration of the activity of 5 wt% Pd/Al_2O_3, but it could be mitigated or avoided by the operation at higher temperatures. By the treatment with 1 vol% isoflurane diluted in air at 300 °C, all the catalysts were irreversibly damaged probably due to the reaction with HF originated from the decomposition of isoflurane. The weight of Al_2O_3-supported catalysts increased because of the conversion of Al_2O_3 to AlF_3, and that of SiO_2-supported catalysts decreased because of the evaporation of SiF_4. The tolerance against the isoflurane treatment depended on the kind of precious metals and Ru was suffered less deactivation than Rh and Pd.

1. Introduction

Nitrous oxide (N_2O) has been long considered as a relatively harmless species. During the last decade, however, the environmental impact of N_2O has been noticed; it contributes to both the greenhouse effect and the stratospheric ozone destruction [1–3] and it is one of longest lived pollutants with about 150 years of a life span in atmosphere. Accordingly, the control of N_2O emission is becoming an important field in the environmental technology. The catalytic decomposition of N_2O into N_2 and O_2 seems to be the easiest way to control N_2O emission. So far, various types of catalysts have been reported to be active for the decomposition of N_2O. Li and Armor [2] reported that Rh/ZSM-5 catalyst was very active for the catalytic decomposition of N_2O at low temperature (e.g., 300 °C). Oi et al. [4] have studied the activities of various metal-oxide supported Rh catalysts, and concluded that Rh/ZnO was the most active catalyst. Several works [5–7] have reported for the catalytic decomposition of N_2O over Al_2O_3 supported precious metals (Rh, Ru, Ir) catalysts. However, the catalytic activity for decomposition of N_2O was significantly affected by various coexisting gases, such as O_2, H_2O, and CH_4 [7–9].

N_2O is widely used in surgical operations as an anesthetic gas. The anesthetic gas is composed of nearly equal amounts of N_2O and O_2 and 1–2 vol% volatile anesthetics which are halogenated ethers such as isoflurane ($CHF_2OCHClCF_3$, 2-chloro-2-(difluoromethoxy)-1,1,1-trifluoro-ethane) and sevoflurane ($CH_2FOCH(CF_3)_2$, 2,2,2-trifluoro-1-[trifluoromethyl]ethyl fluoromethyl ether). The used anesthetic gas is exhausted to the outside of the operation room without any treatments through an anesthetic gas scavenging system (AGSS). Since it is impossible to perfectly scavenge the anesthetic gas by the AGSS system, the leakage of a small amount of the anesthetic gas happens in the operation room. Doi et al. [10] have been studied the catalytic decomposition of N_2O to purify the leaked anesthetic gas in medical operating rooms, and they used the reaction mixture of 21% O_2, 79% N_2, 60 ppm N_2O, 7000 and 5 ppm ethanol and <50 ppm isoflurane. They have concluded that Rh/Al_2O_3 catalyst is suitable to decompose N_2O in operating rooms. The N_2O decomposition activity of Rh/Al_2O_3 dropped sharply when isoflurane was added in the reaction gas, and it recovered after the removal of isoflurane. Therefore, the impact of isoflurane was reported to be reversible when its concentration was low.

The purpose of this study is to investigate N_2O decomposition catalysts for the purification system of waste anesthetic gas which

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is placed in the downstream of the AGSS system and abates N_2O emission to atmosphere. In addition to catalyst screening, effects of three gases of O_2, H_2O and isoflurane as a representative of halogenated ethers were investigated because they are inevitably present in the waste anesthetic gas.

2. Experimental

2.1. Catalysts

Commercially available γ-Al_2O_3-supported palladium, rhodium, ruthenium and platinum catalysts, Pd/Al_2O_3 (N.E. CHEMCAT), Rh/Al_2O_3 (Kishida), Ru/Al_2O_3 (Soekawa Chem.) and Pt/Al_2O_3 (ACROS) were used in the present study. Pd/Al_2O_3 catalyst was also prepared by wet-impregnating Al_2O_3 powder (JRC-ALO-4, Catalysis Society of Japan) with an aqueous solution of $Pd(NO_3)_2$ (Kishida). The commercial and home-made Pd/Al_2O_3 catalysts were denoted as Pd/Al_2O_3[C] and Pd/Al_2O_3[H], respectively. Silica-supported catalysts (Pd/SiO_2, Rh/SiO_2, Ru/SiO_2) were prepared by the wet-impregnation with SiO_2 powder (JRC-SIO-4, Catalysis Society of Japan) and aqueous solutions of $Pd(NO_3)_2$ (N.E.CHEMCAT), $Rh(NO_3)_3$ (Kishida), $Ru(NO_3)_3$ (Soekawa Chem.). After evaporation-to-dryness, the catalysts were dried at 110 °C and calcinated at 500 °C for 2 h in air. The loading of precious metals (Pd, Rh and Ru) was fixed at 5 wt%.

2.2. Characterization of catalysts

Specific surface areas were measured by the BET method (Gemini 2375, Micromeritics). Catalysts were degassed at 300 °C for 1 h at a base pressure of 10^{-3} Torr before the nitrogen adsorption measurement at 77 K. The crystal structure of catalysts was examined by powder X-ray diffraction method (RINT2200, Rigaku) using Cu Kα radiation.

2.3. Evaluation of N_2O decomposition activity

The catalytic reaction of N_2O decomposition was carried out in a fixed-bed flow reactor by feeding a model reaction gas, N_2O (5 vol%)–O_2 (5 vol%)–He (balance), feeding at a rate of 50 $cm^3\ min^{-1}$. The granulated catalysts (180–355 μm, 0.2 g) was packed in a reactor, and pretreated at 500 °C for 0.5 h in a stream of 20 vol% O_2 balanced with He at a total flow rate of 30 $cm^3\ min^{-1}$. The catalytic activity was measured by the temperature programmed reaction (TPR) method. The temperature of the catalyst bed was raised from room temperature to 600 °C at a rate of 4 °C min^{-1} by an electric furnace. The outlet gas was analyzed with intervals of 7–8 min (28–32 °C) by an online TCD gas chromatograph (GC-14A, SHIMADZU) equipped with columns of Porapack Q (for the analysis of N_2O) and Molecular Sieve 5A (for that of O_2 and N_2). The catalytic activity was evaluated in terms of the conversion (X) of N_2O according to the following equation:

$$X = \left\{ \frac{[N_2O]_{in} - [N_2O]_{out}}{[N_2O]_{in}} \right\} \times 100 \qquad (1)$$

where $[N_2O]_{in}$ and $[N_2O]_{out}$ are concentrations of N_2O in inlet and outlet gases, respectively.

The influences of coexisting O_2 and H_2O were evaluated by changing O_2 concentration (0–20 vol%) and additionally feeding H_2O (0–*ca.* 3 vol%), respectively. The impact of isoflurane was evaluated by comparison of activity before and after the isoflurane-treatment in which catalysts were exposed to 1% isoflurane in air at 300 °C for 30 min. The regeneration of the isoflurane-treated catalysts was carried out by the heat-treatment at 700 °C for 30 min in 20 vol% O_2 balanced with He.

3. Results and discussion

3.1. N_2O decomposition activity of Pd/Al_2O_3 catalysts

Fig. 1 shows temperature dependence of N_2O decomposition over fresh 5 wt% Pd/Al_2O_3[C]. In the TPR run, the concentration of N_2O started to decrease at 200 °C and became zero above 300 °C. In the same temperature range, N_2 and O_2 were produced in the ratio of 2:1. These results clearly show the occurrence of the direct decomposition of N_2O in the presence of O_2. Also shown in Fig. 1 is N_2O concentration observed in a steady-state reaction (SSR) in which the N_2O concentration was measured after reaching the steady state at each temperature and the stoichiometric formations of N_2 and O_2 were also conformed. Above N_2O concentration of *ca.* 4 vol%, in other words, below the conversion of *ca.* 20%, the TPR method gave the higher conversion than the SSR method. At the conversion above *ca.* 20%, on the other hand, both methods gave the comparable conversion. It is true that the real catalytic activity should be evaluated by the SSR method and that the TPR method overestimates the activity below *ca.* 20% conversion under the present condition. The TPR method, however, was sufficient in the present study which aimed to compare the ability to decompose N_2O of several catalysts and to evaluate effects of coexisting gases.

Fig. 2 compares N_2O decomposition activity between fresh Pd/Al_2O_3[C] and Pd/Al_2O_3[H]. It can be seen that the former catalyst is more active than the latter. The specific surface area of Pd/Al_2O_3[C] (118 $m^2\ g^{-1}$) was smaller than that of Pd/Al_2O_3[H] (172 $m^2\ g^{-1}$). XRD patterns of fresh 5 wt% Pd/Al_2O_3 catalysts are shown in Fig. 3. No XRD peaks originated from Pd species were observed for Pd/Al_2O_3[C], indicating that Pd species are well dispersed on alumina support and the crystalline size is too small to be detected by XRD. For home-made Pd/Al_2O_3[H] catalyst, on the other hand, XRD peaks ascribable to PdO were observed. Although the dispersion of Pd was not directly measured by, for example, CO or H_2 adsorption, it can be easily understood from XRD results that the dispersion of Pd species (PdO) in Pd/Al_2O_3[C] is higher than that in Pd/Al_2O_3[H]. Therefore, the higher activity of Pd/Al_2O_3[C] can be reasonably ascribable to the higher dispersion of Pd species.

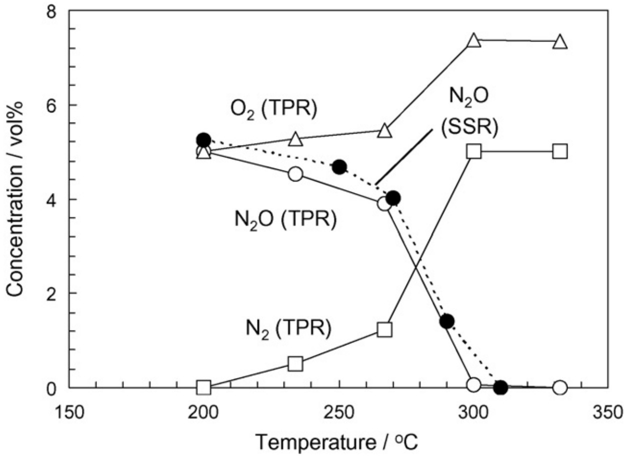

Fig. 1. Temperature dependence of N_2O decomposition over 5 wt% Pd/Al_2O_3[C] catalyst as a function of temperature. Open and closed symbols are results obtained in the temperature programmed reaction (TPR) at a ramping rate of 4 °C min^{-1} and the steady-state reaction (SSR), respectively. *Reaction gas*: N_2O (5 vol%)–O_2 (5 vol%)–He (balance).

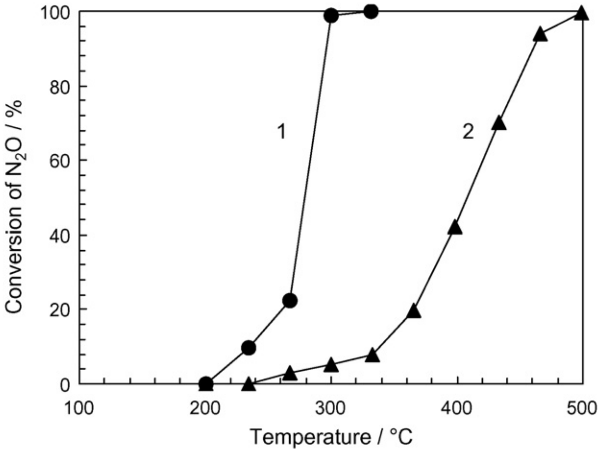

Fig. 2. N_2O conversion on fresh (1) 5 wt% Pd/Al_2O_3[C] and (2) 5 wt% Pd/Al_2O_3[H] catalysts as a function of catalyst temperature. *Reaction gas*: N_2O (5 vol%)–O_2 (5 vol%)–He (balance).

3.2. *Influences of coexisting O_2 and H_2O*

The effect of concentration of O_2 on N_2O decomposition activity was examined with the fresh 5 wt% Pd/Al_2O_3[C] catalyst. Fig. 4 shows the conversion of N_2O at 270, 290 and 310 °C as a function of concentration of coexisting O_2. The activity tended to decrease with an increase in oxygen concentration up to 20 vol%, but it can be said that the activity was very slightly affected by coexisting O_2. This result shows that the direct decomposition of N_2O is possible in the presence of O_2 even though O_2 is a reaction product.

Fig. 5 shows the effect of concentration of H_2O on N_2O decomposition activity of the fresh 5 wt% Pd/Al_2O_3[C] catalyst. At 300 °C, the conversion in the absence of H_2O was 100%. When 1.2 vol% H_2O was added to the reaction gas, the conversion dropped suddenly to about 10%. With increasing the temperature of the catalyst bed, the deterioration effect of H_2O became small and almost disappeared above 350 °C. The coexisting H_2O damaged the activity presumably due to the adsorption on and blockage of active sites, but it can be avoided by increasing temperature. It was confirmed that the coexisting H_2O did not cause the permanent deactivation.

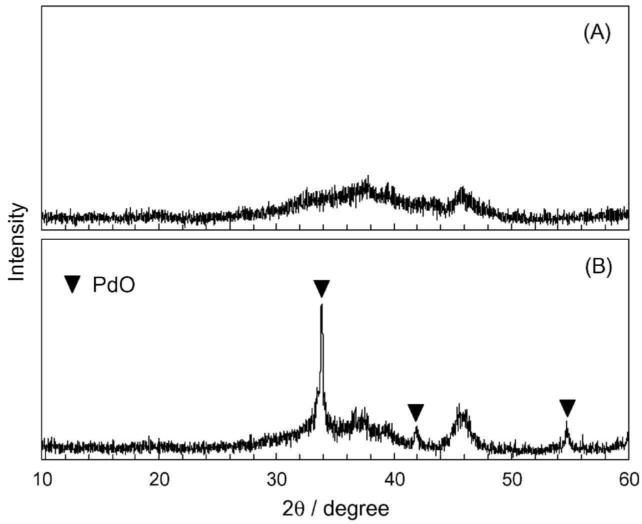

Fig. 3. X-ray diffraction patterns of fresh (A) 5 wt% Pd/Al_2O_3[C] and (B) 5 wt% Pd/Al_2O_3[H].

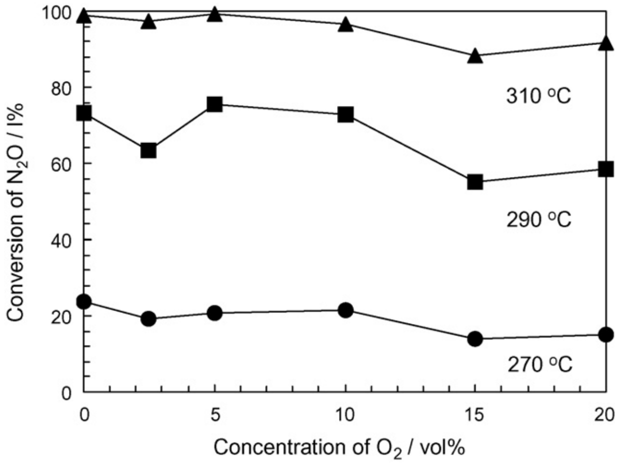

Fig. 4. The effect of concentration of coexisting O_2 on N_2O decomposition activity of 5 wt% Pd/Al_2O_3[C]. *Reaction gas*: N_2O (5 vol%)–O_2 (variable)–He (balance).

3.3. *N_2O decomposition activity of various supported precious metal catalysts*

In Sections 3.1 and 3.2, it has turned out that the direct decomposition of N_2O is possible with 5 wt% Pd/Al_2O_3[C] in the presence of O_2 and H_2O. After the isoflurane-treatment, however, the catalyst severely deactivated as described in the next section. Therefore, N_2O decomposition activities of various precious metal catalysts supported on Al_2O_3 and SiO_2 were measured. Fig. 6(A) shows the results of fresh catalysts. Rh/Al_2O_3 was the most active among the fresh catalysts investigated, followed by Pd/Al_2O_3[C], Rh/SiO_2, Ru/SiO_2, Ru/Al_2O_3 and Pd/SiO_2. Pt/Al_2O_3 was far less active than the other catalysts. Although the activity is dependent on the dispersion of the precious metals as evidenced in Pd/Al_2O_3 (Section 3.1), Rh gave the highest activity for the N_2O decomposition in the present study, which is in accordance with previously reported result [10].

3.4. *Influence of a halogenated ether (isoflurane)*

Halogenated ethers are inevitably contained in the waste anesthetic gas from the operation room. Doi et al. reported the

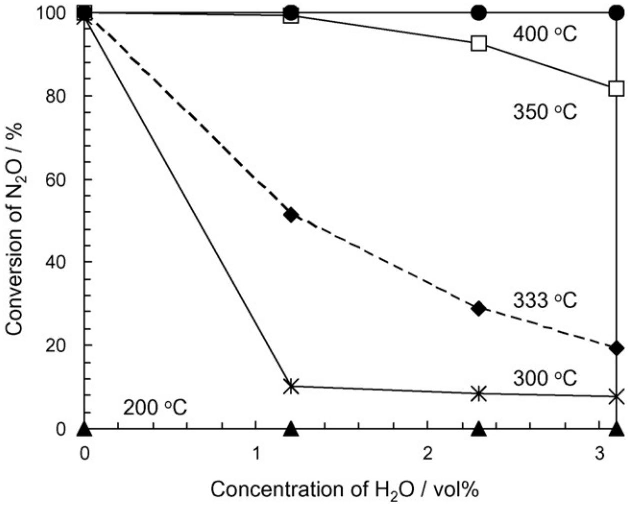

Fig. 5. The effect of concentration of coexisting H_2O on N_2O decomposition activity of 5 wt% Pd/Al_2O_3[C]. *Reaction gas*: N_2O (5 vol%)–O_2 (5 vol%)–H_2O (variable)–He (balance).

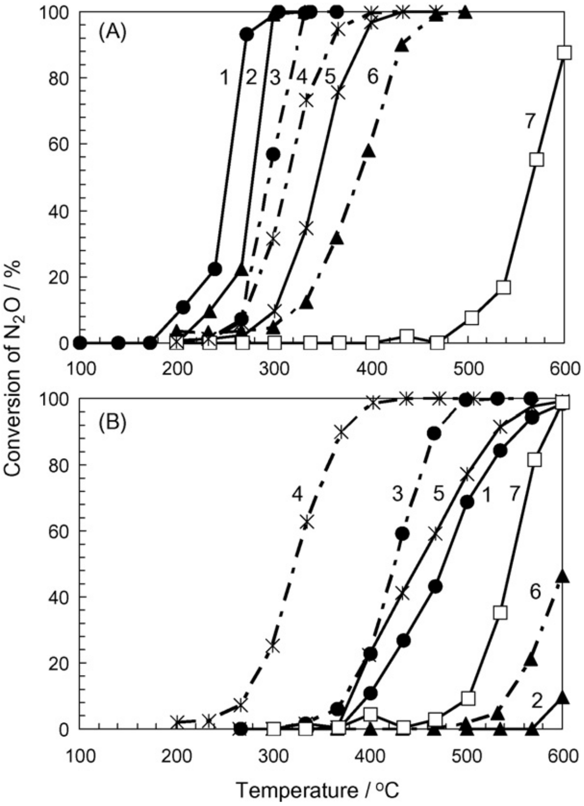

Fig. 6. Temperature dependence of N_2O decomposition activity of 5 wt% precious metal catalysts supported on Al_2O_3 and SiO_2. (A) Fresh catalysts, (B) isoflurane-treated catalysts. (1) Rh/Al_2O_3, (2) Pd/Al_2O_3[C], (3) Rh/SiO_2, (4) Ru/SiO_2, (5) Ru/Al_2O_3, (6) Pd/SiO_2, (7) Pt/Al_2O_3. *Reaction gas*: N_2O (5 vol%)–O_2 (5 vol%)–He (balance).

impact of isoflurane, representative halogenated ether, on N_2O decomposition activity of Rh/Al_2O_3 [10]. They used very low concentration of isoflurane below 50 ppm because the target was the development of the catalyst for the purification of anesthetic gas leaked into the operation room. For the treatment of waste anesthetic gas in the exhaust line, on the other hand, the effect of halogenated ethers in higher concentrations should be evaluated. In addition, the stability of the catalyst against the ether should be also examined. Therefore, 1% of isoflurane was used in this study, and its influence was investigated by comparison of the activity before and after the isoflurane-treatment at 300 °C.

Fig. 6(B) shows N_2O decomposition activity of the isoflurane-treated catalysts. The effects of the isoflurane-treatment on the N_2O decomposition activity and specific surface area are summarized in Table 1. Except for 5 wt% Ru/SiO_2, the catalysts severely deactivated by the isoflurane-treatment. Alumina-supported catalysts suffered more deactivation than silica-supported ones; for example, decrements of temperature giving 50% conversion of N_2O (ΔT_{50}) by the isoflurane-treatment were 226 and 132 °C for Rh/Al_2O_3 and Rh/SiO_2, respectively, and 106 and 9 °C for Ru/Al_2O_3 and Ru/SiO_2, respectively. The specific surface areas of alumina-supported catalysts were largely decreased by the isoflurane-treatment, but those of silica-supported catalysts slightly decreased (Ru/SiO_2) or increased (Rh, Pd/SiO_2). XRD patterns of the fresh and isoflurane-treated Ru/Al_2O_3 are shown in Fig. 7. For the isoflurane-treated catalyst, the presence of AlF_3 and RuO_2 were confirmed. The formation of AlF_3 suggests that hydrogen fluoride is formed by the decomposition of isoflurane and it reacts with Al_2O_3 to form AlF_3.

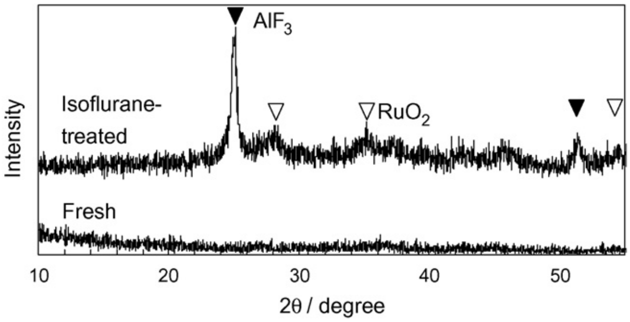

Fig. 7. X-ray diffraction patterns of fresh and isoflurane-treated 5 wt% Ru/Al_2O_3.

$$Al_2O_3(s) + 6HF \rightarrow 2AlF_3(s) + 3H_2O \tag{2}$$

The conversion of Al_2O_3 into AlF_3 seems to cause the decrease in surface area and therefore the growth (aggregation) of RuO_2 to the size detectable by XRD. The oxide–fluoride conversion was not clearly observed for alumina-supported Pd/Al_2O_3 and Rh/Al_2O_3. However, the oxide–fluoride conversion is considered to occur because the weight increase during the isoflurane-treatment was observed for Rh/Al_2O_3 and Pd/Al_2O_3. As for SiO_2-supported catalysts, the isoflurane-treatment caused no obvious change of XRD patterns for both the support and precious metals. This might be reasonable because the decrease in specific surface area which brings about the growth of supported species was not observed, as mentioned above. The weight of SiO_2-supported catalysts was found to decrease during the isoflurane-treatment (Table 1). Fig. 8 shows the change in weight during the isoflurane-treatment up to 15 h. After the fast decrease up to 3 h, the weight steady decreased with increasing the time for the isoflurane-treatment. SiO_2 reacts

Table 1
Effect of isoflurane-treatment on N_2O decomposition activity of 5 wt% precious metal catalysts supported on Al_2O_3 and SiO_2

Catalyst	T_{50}[a] (°C)			Specific surface area ($m^2\ g^{-1}$)		Weight change[e]
	F[b]	IT[c]	R[d]	F[b]	IT[c]	
Rh/Al_2O_3	252	478	615	117	61	+3.9% (1 h)
Pd/Al_2O_3[C]	277	$\gg$600	n.m.[f]	118	51	+5.3% (0.5 h)
Ru/Al_2O_3	345	451	559	154	40	n.m.[f]
Pt/Al_2O_3	498	n.m.[f]	n.m.[f]	163	n.m.[f]	n.m.[f]
Rh/SiO_2	293	425	315	169	180	−2.6% (1 h)
Ru/SiO_2	314	323	308	270	266	−3.0% (0.5 h)
Pd/SiO_2	389	$\geq$600	524	181	184	−0.7% (1 h)

[a] Temperature giving 50% conversion of N_2O.
[b] Fresh catalyst.
[c] Isoflurane-treated catalyst.
[d] Regenerated catalyst.
[e] Weight change during the isoflurane treatment. Treatment time is shown in parentheses.
[f] Not measured.

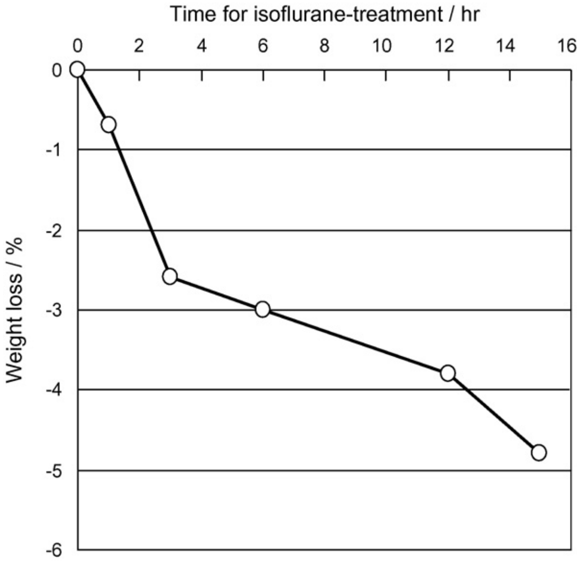

Fig. 8. Weight change of 5 wt% Pd/SiO_2 during the isoflurane-treatment.

with hydrogen fluoride formed by the decomposition of isoflurane as in the case of Al_2O_3.

$$SiO_2(s) + 4HF \rightarrow SiF_4(g) + 2H_2O \qquad (3)$$

The reaction product of SiF_4 is a gaseous compound under the present condition, and therefore the vaporization as SiF_4 seems to be a reason for the weight loss.

The regeneration of the catalysts deactivated by the isoflurane treatment was attempted by the heat-treatment in 20 vol% O_2 in He. The effect of regeneration temperature above 500 °C was studied on 5 wt% Rh/SiO_2. As shown in Table 1, T_{50} values were 293 and 425 °C for the fresh and deactivated catalysts. The regeneration at 500 and 600 °C caused a slight increase of the activity with T_{50} of 405 and 383 °C, respectively. After the regeneration treatment at 700 °C, the catalyst recovered the activity with T_{50} of 315 °C which was slightly lower than that of the fresh catalyst. Therefore, the regeneration was carried out at 700 °C and the T_{50} values of regenerated catalysts are listed in Table 1. The regeneration treatment at 700 °C resulted in the recovery of the activity of SiO_2-supported catalysts although the degree of the recovery was different for the different catalysts. As for the Al_2O_3-supported catalysts, on the other hand, the regeneration treatments caused further deactivation. By the isoflurane-treatment on the SiO_2-suppported catalysts, vaporization as SiF_4 occurred but the severe damage hardly did on the remaining solid support (SiO_2) as one can imagine from a little change of the specific surface area. For Al_2O_3-supported catalysts, on the other hand, irreversible conversion of the solid support from oxide to fluoride took place. These differences in the change of the support materials might be a reason for the difference in the regeneration behavior.

As for the effect of precious metals, Pd was the most severely damaged, followed by Rh and Ru for both Al_2O_3- and SiO_2-supported catalysts. Differences in T_{50} between the isoflurane-treated and fresh catalysts were $\gg$323 °C (Pd), 226 °C (Rh) and 106 °C (Ru) for Al_2O_3-supported catalysts and $\geq$211 °C (Pd), 132 °C (Rh) and 9 °C (Ru) for SiO_2-supported catalysts. According to Doi et al. [10], the deactivation of Rh/Al_2O_3 by the presence of isoflurane is caused by the strong adsorption of F on Rh surface. Therefore, the difference in damage by the isoflurane treatment might be resulted from the difference in the adsorption strength of F on the metal surface.

It has turned out that the all the catalysts investigated in this study cannot tolerate the treatment by an F-containing ether because of the reaction with HF. Ru/SiO_2 seemed to have tolerance against the F-containing ether only judging from the N_2O decomposition activity, but the irreversible change, that is, the weight loss of SiO_2 took place. Therefore, it has been suggested that removal of the ethers before entering the catalyst bed is indispensable to realize purification system of the waste anesthetic gas using N_2O decomposition catalysts.

4. Conclusions

As a part of development of catalytic system for purifying waste anesthetic gas, the effects of coexisting O_2, H_2O and isoflurane (F-containing ether) on the N_2O decomposition activity of supported precious catalysts were investigated.

The N_2O decomposition activity of 5 wt% Pd/Al_2O_3 was very slightly affected by coexisting O_2 and reversibly deteriorated by coexisting H_2O. When Al_2O_3- and SiO_2-supported precious metal catalysts were treated with isoflurane at 300 °C, all the catalysts were irreversibly damaged because of the conversion of alumina to AlF_3 and the vaporization as SiF_4 and therefore the weight loss of SiO_2. Among the precious metals investigated (Pd, Rh, Ru), Ru was the most tolerant against the isoflurane treatment. Development of catalysts which are stable against F-containing ethers or that of the pre-removal system of the ethers is necessary to realize the waste anesthetic gas purification system.

References

[1] P.L. Crutzen, J. Geophys. Res. 76 (1971) 7311.
[2] Y. Li, J. Armor, Appl. Catal. B 1 (1992) L21.
[3] J.C. Kramlich, W.P. Linak, Prog. Energy Combust. Sci. 20 (1994) 149.
[4] J. Oi, A. Obuchi, G. Bamwenda, A. Ogata, H. Yagita, S. Kushiyama, K. Mizuno, Appl. Catal. B 12 (1997) 277.
[5] K. Yuzaki, T. Yarimizu, K. Aoyagi, S. Ito, K. Kunimori, Catal. Today 45 (1998) 129.
[6] H.C. Zeng, X.Y. Pang, Appl. Catal. B 13 (1997) 113.
[7] C. Ohnishi, S. Iwamoto, M. Inoue, Chem. Eng. Sci. (available on line 19 August 2007).
[8] X.F. Wang, H.C. Zeng, Appl. Catal. B 17 (1998) 89.
[9] A. Satsuma, H. Maeshima, K. watanabe, K. Suzuki, T. Hattori, Catal. Today 63 (2000) 347.
[10] K. Doi, Y.Y. Wu, R. Takeda, A. Matsunami, N. Arai, T. Tagawa, S. Goto, Appl. Catal. B 35 (2001) 43–51.