

Catalytic Decomposition of N₂O over Rhodium-Loaded Metal Oxides

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The catalytic decomposition of dinitrogen oxide to nitrogen and oxygen was studied over various rhodium-loaded metal oxides. Rh/ZnO was found to have the highest activity. The effects of metal loading and calcination conditions upon the catalytic performance were also examined. An air-pretreated 0.5 wt% Rh/ZnO was found to be the most active catalyst with a reaction rate of $4.0 \times 10^4 \mu\text{mol}(\text{N}_2\text{O}) \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ under conditions of 950 ppm of N₂O and 5% of O₂ at 300 °C.

The catalytic decomposition of N₂O has been widely studied since N₂O is one of the pollutants contributing to the greenhouse effect and the depletion of the ozone layer.¹⁻⁴ Recently, Li et al. studied various metal exchanged zeolites as a catalyst for the N₂O decomposition.¹ At 400 °C and a space velocity of 30000 h⁻¹, they obtained a reaction rate of $2.7 \times 10^3 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ on Cu/ZSM-5. They also reported rhodium has very high activity for N₂O decomposition. Herein we report the catalytic activity of N₂O decomposition over various Rh-loaded metal oxides. We found that the combination of rhodium and zinc oxide was efficient for this reaction.

Catalysts made of 1 wt% Rh supported on various oxides, as listed in Table 1, were prepared by the impregnation method. Usually Rh(NO₃)₃ was used as a precursor. Rh/ZnO (0.1 wt%~2 wt%) was synthesized by the same method using Rh(NO₃)₃ and ZnO (New Jersey Zinc Company; Kadox25, surface area: 10 m²·g⁻¹) and calcined at 500 °C in three kinds of atmospheres: air, nitrogen and hydrogen. Prior to use, the catalysts were pre-treated in 21% O₂ / He mixture at 500 °C for 1h before reaction, to avoid the occurrence of non-catalytic N₂O reduction to N₂ by reduced rhodium surface and to minimize variation in the catalytic activity. The reaction of N₂O decomposition was usually carried out in a continuous flow reactor under the conditions of 950 ppm N₂O and 5% O₂ at temperatures between 150 and 500 °C. The rates of N₂O decomposition were expressed as the moles of N₂O reacted per hour per gram catalyst at 300 °C, which was estimated by interpolation or extrapolation of the Arrhenius plots at low N₂O conversion.

Figure 1 shows N₂O conversion on several Rh catalysts as a function of temperature and Table 1 summarizes the activities of all the catalysts examined, along with those for two catalysts reported in the literatures. Rh/ZnO exhibited the highest activity of $6.0 \times 10^3 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ among the fourteen kinds of catalysts examined. Although differences in experimental conditions on

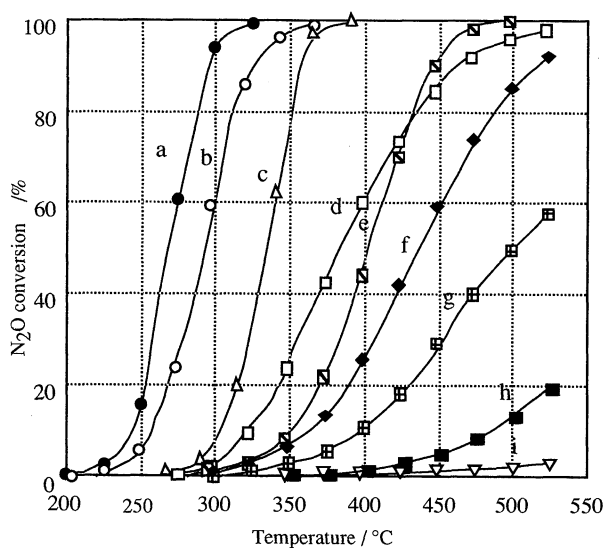


Figure 1. N₂O decomposition on various 1 wt% Rh loaded oxides as a function of temperature. Calcination conditions: 500 °C, H₂, 2 h. The reactions were run on a 0.1 g of sample with a total flow rate of 80 ml·min⁻¹ for a, b, h, 160 ml·min⁻¹ for d, e, f, g, i, and 40 ml·min⁻¹ for c, and [N₂O] = 950 ppm, [O₂] = 5%, He-balance.
 a:Rh/ZnO, b:Rh/ZSM-5, c:Rh/MgAl₂O₄, d:Rh/CeO₂, e:Rh/Al₂O₃, f:Rh/ZrO₂, g:Rh/Yb₂O₃, h:Rh/NiO, i:Rh/SiO₂

Table 1. Comparison of catalytic activities for N₂O decomposition in terms of the rate

No.	Catalyst	Activity ^a
1	Rh / ZnO	6.0×10^3
2	Rh / ZSM-5	5.4×10^2
3	Rh / CeO ₂	1.1×10^2
4	Rh / MgAl ₂ O ₄	7.4×10^1
5	Rh / Al ₂ O ₃	6.4×10^1
6	Rh / ZrO ₂	1.0×10^1
7	Rh / Yb ₂ O ₃	8.4×10^0
8	Rh / SiO ₂	6.1×10^0
9	Rh / NiO	1.0×10^0
10	Rh / TiO ₂	4.7×10^{-1}
11	Rh / Gd ₂ O ₃	2.5×10^{-2}
12	Rh / La ₂ O ₃	6.1×10^{-3}
13	Rh / WO ₃	2.5×10^{-3}
14	Rh / MgO	4.0×10^{-4}
ref.	0.6 wt% Rh / ZSM-5 ^b	1.9×10^3
ref.	Ni-Al-CO ₃ -HT ^c	7.8×10^1

^a $\mu\text{mol}(\text{N}_2\text{O}) \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at 300 °C

^b estimated from a figure in reference 1; under conditions of 990 ppm N₂O in the absence of O₂.

^c estimated from activation energy and frequency factor in reference 2.

Rh loading: 1wt%, Calcination conditions: 500 °C in H₂, 2 h.

The reactions were run on a 0.1 g of sample with a total flow rate of 80 ml·min⁻¹ for No. 1, 2, 9, 14, 160 ml·min⁻¹ for No. 3, 5-8, 10-13 and 40 ml·min⁻¹ for No. 4, and [N₂O] = 950 ppm, [O₂] = 5%, He-balance.

Table 2. Dependence of catalytic activities of Rh / ZnO catalysts on the calcination atmosphere and Rh loading

Catalyst	Pretreatment atmosphere	Rh load. (wt%)	Activity ^a
Rh / ZnO	air	2.0	4.0×10^3
		1.0	1.5×10^4
		0.5	4.0×10^4
		0.1	1.1×10^4
N ₂		1.0	6.6×10^3
		0.5	3.3×10^4
		0.1	5.5×10^3
H ₂		1.0	6.0×10^3
		0.5	1.8×10^4
		0.1	4.5×10^3

^a $\mu\text{mol (N}_2\text{O)} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at 300 °C

Calcination conditions: 500 °C, 2 h.

The reactions were run on a 0.1g of sample with a total flow rate of 80 ml·min⁻¹ and [N₂O] = 950 ppm, [O₂] = 5%, He-balance.

each catalyst do not allow us to strictly compare the activities, Rh/ZnO was estimated to be even more active than Rh/ZSM-5

reported by Li et al.¹ and Ni-Al supported on hydrotalsite-like compounds (Ni-Al-CO₃-HT) by Kannan et al.²

Table 2 shows the dependence of the catalytic activities of Rh/ZnO on the calcination atmosphere and metal loading. The most effective calcination media was air, whereas the activities of the samples calcined in hydrogen were rather low. This strongly suggests that the effective form of rhodium for N₂O decomposition is an oxidized one. Interestingly, the most effective loading was 0.5wt% in every calcination atmosphere. 0.5 wt% Rh/ZnO calcined in air exhibited the reaction rate of $4.0 \times 10^4 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at 300 °C for the reactant containing 950 ppm of N₂O and 5% of O₂, which was much higher than those reported in the literature.

References and Notes

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