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Photocatalytic Decomposition of N_2O at Room Temperature

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Decomposition of N_2O into N_2 and O_2 at room temperature was demonstrated on a Pt/TiO_2 photocatalyst in the presence of water vapor. The photocatalytic activity was enhanced by the participation of photocatalytic decomposition of water.

Reduction and decomposition reactions of nitric oxides, mainly NO, have been extensively studied in the field of catalysis, especially from the view point of pollution control. Among nitric oxides, N_2O gas is relatively stable under ambient conditions, and causes a green house effect as well as the destruction of the ozone layer. The elimination process of N_2O has not been studied in depth, although it is needed. These nitric oxides are thermodynamically unstable. But it is not kinetically easy to decompose N_2O into N_2 and O_2 at low temperatures (<600 K) even in the presence of catalysts. Furthermore, O_2 is hardly released into a gas phase by decomposition at low temperatures because of adsorption as an oxygen species on a catalyst surface. Therefore, the catalytic decomposition of N_2O into N_2 and O_2 at room temperature is important from industrial and academic view points.

On the other hand, redox reactions, which are usually attended by the electron transfer, proceed under mild conditions by using photocatalysts. It would be reasonable to employ photocatalysts for the decomposition of N_2O because N_2O works as an electron acceptor to form N_2O^- which readily decomposes into N_2 and O^- on a catalyst surface. Some works have been reported on the reduction or decomposition of NO and N_2O on photocatalysts.[1-8] Reducing reagents such as CO and NH_3 are usually used for the reduction reaction.[1b,d,7,8] Among the reports, Tanaka *et al.* have investigated the relation between thermal and photocatalytic decomposition of N_2O and its kinetics on ZnO powder at high temperatures (>650 K) at which thermal catalytic decomposition also proceeded.[1a,c] Cunningham *et al.* have reported photoassisted decomposition of N_2O at room temperature on reduced ZnO powders.[2] Anpo *et al.* have shown the decomposition of N_2O on a clusterlike TiO_2 photocatalyst anchored onto porous Vycor glass and have investigated the N_2O^- radical formation in detail by means of ESR.[5]

In the present study, decomposition of N_2O into N_2 and O_2 at room temperature on photocatalysts (Pt/TiO_2) is presented. The effect of water on the photocatalytic decomposition of N_2O and its dependency on N_2O pressure were investigated.

TiO_2 (Furuuchi Chem. Co., purity; 99.99%) and SiO_2 (Kojundo Chem. Lab. Co., purity; 99.99%) powders were used as received. Pt(1.5 wt%)/TiO_2 and Pt(1.5 wt%)/SiO_2 catalysts were prepared by an impregnation method using an aqueous H_2PtCl_6 solution. Photocatalytic reactions were carried out in a gas-closed circulation system with a flat bottom reaction cell made of Pyrex glass. The platinum-supported catalysts were reduced at 720 K for 1-2 h under hydrogen atmosphere (150 Torr) before usage. A high pressure mercury lamp (Ushio-UM452, 450 W) with a water-cooling jacket was employed as a light source. Amounts of products (N_2 and O_2) were determined by using a gas chromatography (Okura; model 802, molecular sieve 5A column, thermal conductive detector, He carrier).

Figure 1 shows time courses of photocatalytic decomposition of N_2O into N_2 and O_2 on Pt(1.5 wt%)/TiO_2 powder in the presence of water vapor. It is noteworthy that N_2 and O_2 evolved in stoichiometric amounts on the Pt/TiO_2 photocatalyst at room temperature.

Table 1 summarizes the initial activities of N_2O decomposition on some catalysts. A small amount of N_2 (ca. 1.5 μmol) evolved under dark condition in the beginning (<1 h) of contact of N_2O with a fresh Pt/TiO_2 catalyst after reduction treatment. The N_2 evolution is probably due to the stoichiometric reaction of N_2O with platinum and/or reduced TiO_2 surface. In this case, oxygen species were probably left on the surfaces and O_2 did not evolve. The photocatalytic reaction was carried out after this dark reaction had stopped, and the activity was corrected by subtracting the amount of N_2 evolved during the dark reaction.

N_2O did not decompose catalytically on the Pt/TiO_2 photocatalyst in the absence of water (Run 1). In this case, only a small amount of N_2 without O_2 evolution was formed in the beginning of the reaction. The problem in this reaction is that oxygen species remain on the catalyst surface. The photocatalyst became active after it came into contacted with 10 Torr of water and subsequently evacuated at room temperature

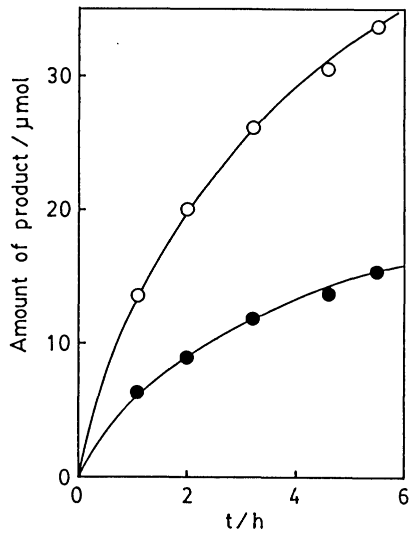

Fig.1. Photocatalytic decomposition of N_2O on Pt(1.5 wt%)/TiO_2 in the presence of water vapor. N_2O; 126 Torr, H_2O; 5 Torr ○ ; N_2, ● ; O_2.

Table 1.
Decomposition of N_2O on photocatalysts

Run	Catalyst[a)]	Reactant (Torr)		Activity[b)] (µmol/h)	
		N_2O	H_2O	N_2	O_2
1	Pt/TiO_2	50	0	1.6	0
2	Pt/TiO_2	50	(10)[c)]	9.0	1.8
3	Pt/TiO_2	50	5	10.6	4.4
4	Pt/TiO_2	50	15	9.6	3.9
5	Pt/TiO_2	50	0[d)]	243	0
6	Pt/TiO_2	50	25[d)]	251	0
7	TiO_2	50	0	0	0
8	TiO_2	50	25	0	0
9	Pt/SiO_2	50	0	0	0
10	Pt/SiO_2	50	25	0	0
11	Pt/TiO_2	50	0[e)]	15.4	0
12	Pt/TiO_2	50	0[f)]	19.6	4.2

a) Catalyst: 1 g, amount of Pt supported: 1.5 wt%, light source; 450 W Hg lamp. b) Initial activity for 1 h after the reaction started. c) Water was evacuated before the reaction. d) Reaction with H_2 (50 Torr) under dark condition. e) Thermal reaction at 620 K. f) Thermal reaction at 720 K.

(Run 2). This suggests that a small amount of water is effective for this reaction. By this water treatment, hydroxyl groups and/or adsorbed water can exist on the catalyst surface. The pressure of water vapor did not considerably affect the activity (Runs 3 and 4). The photocatalytic activity was increased with an increase in the pressure of N_2O (20-126 Torr) in the presence of water. No photocatalytic activities were obtained on Pt(1.5 wt%)/SiO_2 and TiO_2, showing that both Pt and TiO_2 were indispensable (Runs 5-8). Only N_2 was formed on a Pt/TiO_2 catalyst at the initial stage in the thermal reaction at 620 K and the catalytic activity was not obtained (Run 11), suggesting that the thermal effect by irradiation was negligible for the photocatalytic reaction. Under the dark condition, N_2O was reduced to form N_2 with H_2 on the Pt/TiO_2 catalyst in the presence and absence of water (Runs 5 and 6), indicating that adsorbed atomic hydrogen on platinum can reduce N_2O at room temperature. These results suggest the following reaction scheme;

$$TiO_2 + h\nu \rightarrow e^- + h^+, \qquad (1)$$

$$H^+ + e^- \rightarrow H \quad \text{on Pt}, \qquad (2)$$

$$N_2O + 2H \rightarrow N_2 + H_2O \quad \text{on Pt,} \qquad (3)$$
$$N_2O + e^- \rightarrow N_2O^- \quad \text{on Pt,} \qquad (4)$$
$$N_2O^- + H \rightarrow N_2 + OH^- \quad \text{on Pt,} \qquad (5)$$
$$4OH^- + 4h^+ \rightarrow O_2 + 2H_2O \quad \text{on } TiO_2. \qquad (6)$$

Here, e^- and h^+ represent the photogenerated electrons and holes in the conduction band and valence band of TiO_2, respectively. N_2O is reduced by atomic hydrogen formed on a platinum surface by photoreduction of water (Eqs. 1, 2, and 3). It is also possible that N_2O^- is formed by the reaction of N_2O with an electron produced by irradiation of TiO_2 (Eqs. 1 and 4) and is reduced to N_2 (Eq. 5). Platinum works for charge separation of electrons and holes produced in TiO_2 by irradiation and as catalytic sites for dissociation of N_2O. On the other hand, O_2 evolves by photooxidation of water on the TiO_2 surface (Eqs. 1 and 6). Thus, water is cycled and N_2O decomposes into N_2 and O_2 as a whole reaction.

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