Catalysis Letters 52 (1998) 109–111

Photocatalytic reduction of N_2O on metal-supported TiO_2 powder at room temperature in the presence of H_2O and CH_3OH vapor

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Received 13 January 1998; accepted 2 March 1998

Ag- and Cu-supported TiO_2 photocatalysts showed high activity for the reduction of N_2O to N_2 at room temperature in the presence of CH_3OH and H_2O vapor. The suppression by H_2O on the activity was not observed in the present photocatalyst system. The remarkable behavior of the Ag and Cu co-catalysts for TiO_2 photocatalysts agreed well with that of electro- and thermal catalyses.

Keywords: photocatalysis, N_2O, nitrous oxide, Ag/TiO_2, Cu/TiO_2

1. Introduction

N_2O is well known as a greenhouse effect gas as well as CO_2 and CH_4. The development of the emission control process has urgently been desired. On the other hand, N_2O is kinetically stable among nitrogen oxides and, therefore, the activation under mild conditions is an interesting project. N_2O can decompose on some photocatalysts [1–5]. ZnO powder [1,2], and metal oxides [3] and metal ions [5] fixed on suitable supports have mainly been used as photocatalysts. However, semiconductor photocatalysts loaded with co-catalysts have hardly been employed for the N_2O reduction [4]. A drastic effect of co-catalysts is expected for the photocatalytic reduction of N_2O. On the other hand, electrocatalyses for the N_2O reduction have been studied [6–8]. The current efficiency strongly depends on the electrode material showing the remarkable electrocatalyses. Here, the supported photocatalysts are regarded as micro cells. Therefore, the relationship between the electro- and photocatalyses is of interest. This paper reports the efficient reduction of N_2O on some semiconductor photocatalysts loaded with co-catalysts. The mechanism of the photocatalytic activity is discussed by the comparison with electrocatalyses and thermal catalyses.

2. Experimental

The following oxide semiconductor powders were employed: TiO_2 (Kanto, Anatase, purity: 99%), TiO_2 (Kanto, Rutile, purity: 99%), $SrTiO_3$ (Soekawa, purity: 99.9%), WO_3 (Nacalai tesk, purity: 99.5%), Fe_2O_3 (Kanto, purity: 95%), ZnO (Kanto, purity: 99%), In_2O_3 (Kanto, purity: 99.9%), PbO (Kanto, purity: 99%), and $K_4Nb_6O_{17}$ (prepared from K_2CO_3 and Nb_2O_5). Supported catalysts were prepared by an impregnation method using aqueous metal nitrate and chloride solutions. The amounts of metal supported were 0.8–1 wt%. Some photocatalysts were reduced under H_2 flow (1 atm) as pretreatment. However, the pretreated catalysts were contacted with air before use in order to transport it into a reaction cell. The photocatalytic reaction was carried out in a gas-closed circulation system (the dead volume: 210 ml). Photocatalysts (1 g) were scattered in a quartz cell with a flat bottom. 100, 115, and 20 Torr of N_2O, CH_3OH, and H_2O vapor were introduced in the system, respectively, and UV-light was irradiated from upside using a 300 W Xe illuminator (CERMAX, LX300). It is the gas–solid-phase photocatalytic reaction. N_2 evolved was determined using a gas chromatograph (Shimadzu GC-8A, TCD, He carrier).

3. Results and discussion

Table 1 shows the photocatalytic reduction of N_2O on various oxide semiconductor photocatalysts loaded with Ag in the presence of CH_3OH and H_2O vapor. TiO_2, $SrTiO_3$, and $K_4Nb_6O_{17}$ showed reasonable activities. In contrast, ZnO [9] and WO_3 [10], which have been reported to possess photocatalytic activities for O_2 evolution in the presence of Ag^+ and Fe^{3+} as electron scavengers, showed low or negligible activities for the N_2O reduction. TiO_2, $SrTiO_3$, and $K_4Nb_6O_{17}$ photocatalysts can efficiently produce H_2 from water [11]. Therefore, the potentials of water reduction (i.e., the conduction band levels) of photocatalysts seem to be an important factor for the N_2O reduction. This is also supported by the fact that an anatase showed higher activities than a rutile of which the conduction band level is 0.2 eV lower than that of the anatase. The N_2O reduction could easily proceed thermodynamically judging from the considerably positive redox potential, as shown in equation (1).

$$N_2O + 2H^+ + 2e^- \to N_2 + H_2O \quad E^o = +1.77\ \mathrm{V} \quad (1)$$

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Table 1

Photocatalytic N_2O reduction in the presence of CH_3OH and H_2O vapor on various metal oxide semiconductor powders loaded with 1 wt% of Ag.

Catalyst	Pretreatment[a]	Activity of N_2 formation (μmol/h)
TiO_2 (Anatase)	no	171
TiO_2 (Rutile)	no	126
TiO_2 (Rutile)[b]	no	117
TiO_2 (Rutile)[c]	no	0
$SrTiO_3$	no	87
Fe_2O_3	no	0.8
ZnO	yes	3.7
Nb_2O_5	no	6.8
$K_4Nb_6O_{17}$	yes	20
In_2O_3	no	0.3
WO_3	no	0.1
PbO	no	0.3

[a] H_2 reduction at 370 K; [b] without H_2O vapor; [c] in aqueous CH_3OH solution. Catalyst: 1 g; N_2O: 100 Torr; H_2O: 20 Torr; CH_3OH: 115 Torr.

Table 2

Photocatalytic N_2O reduction in the presence of CH_3OH and H_2O vapor on various metals- and metal oxides-supported TiO_2.

Supported co-catalyst[a]	Pretreatment temperature[b] (K)	Activity of N_2 formation (μmol/h)
V_2O_5	no	0.3
Cr oxide	670	0.4
Mn oxide	670	0.2
Fe	670	0.3
Co	670	0.3
Ni	670	0.5
Cu	370	86
ZnO	no	0.3
Ru	470	8.1
Pd	370	0.4
Ag	370	200
Pt	370	0.2
Au	470	0.3

[a] The amounts loaded: Pd: 0.8 wt%, others: 1 wt%; [b] H_2 reduction. Catalyst: 1 g; N_2O: 100 Torr; H_2O: 20 Torr; CH_3OH: 115 Torr.

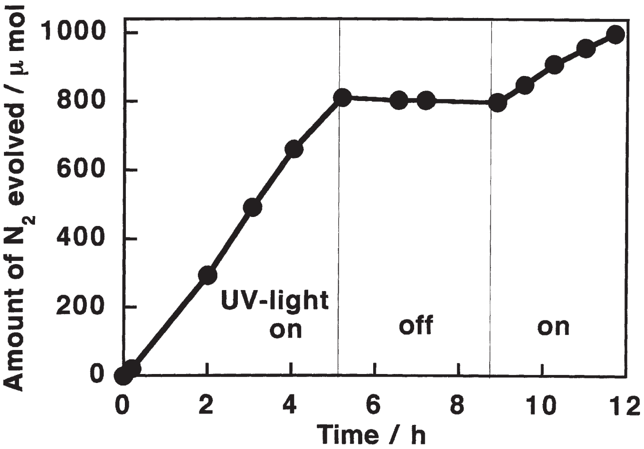

Figure 1. Photocatalytic reduction of N_2O to N_2 on Ag(1 wt%)/TiO_2 powder in the presence of CH_3OH and H_2O vapor. Catalyst: 1 g; N_2O: 100 Torr; H_2O: 20 Torr; CH_3OH: 115 Torr.

However, such a high conduction band level should be indispensable for the N_2O reduction since the process of H^+ reduction is involved in the half reaction.

In the thermal catalytic reduction of nitrogen oxides, in general, the strong suppression by H_2O on the activity is observed. It is noteworthy that the photocatalytic reduction of N_2O efficiently proceeds on the Ag/TiO_2 catalyst even in the presence of H_2O vapor as shown in table 1. However, the photocatalytic reaction at the liquid–solid interface did not proceed when the Ag/TiO_2 photocatalyst was dispersed in an aqueous methanol solution. Thus, the gas–solid interface reaction could cause the high photocatalytic activity.

Figure 1 shows the time course of the photocatalytic reduction of N_2O on the Ag/TiO_2 powder. The amount of N_2 evolved increased with irradiation time and the reaction stopped under dark, indicating that the reaction proceeded photocatalytically.

Table 2 shows the N_2O reduction on various co-catalysts-supported TiO_2 photocatalysts. Ag- and Cu-supported TiO_2 photocatalysts showed high activities while others showed negligible activities. Pt/TiO_2, which has often been used for various photocatalytic reactions, hardly showed activity for the N_2O reduction. In this case, H_2 evolution was predominant. Thus, the remarkable effect of the Ag and Cu co-catalysts supported was observed.

H_2 evolution reactions from aqueous methanol solutions on Pt/TiO_2 photocatalysts are well known to proceed with high quantum efficiencies of several tens percent [11]. The activity for the H_2 evolution from CH_3OH and H_2O vapor on the Pt/TiO_2 photocatalyst was 340 μmol/h under the present experimental conditions. On the other hand, maximum activity of 200 μmol/h for the N_2 evolution from N_2O, CH_3OH and H_2O vapor was obtained when Ag/TiO_2 photocatalysts reduced at 370 K in an H_2 stream was employed, as shown in table 2. The comparison of the activity for the N_2 evolution with that for the H_2 evolution indicates that the efficiency of the Ag/TiO_2 photocatalyst for the N_2O reduction by CH_3OH is considerably high.

In the electrochemical reduction of N_2O in aqueous solutions, Ag and Cu electrodes can reduce N_2O to N_2 with high current efficiencies while H_2 evolution is predominant on a Pt electrode [8]. The electrocatalytic behavior agrees well with the photocatalysis mentioned above. It is interesting that N_2O is hardly reduced on the Pt electrode and the Pt co-catalyst supported on TiO_2 photocatalysts even though nascent hydrogen exists on the surface.

In the thermal catalyses, the titration by N_2O is often employed for the determination of the surface areas of Cu and Ag catalysts [12,13]. This method is based on the following reaction:

$$N_2O \rightarrow N_2 + O_{(ad)} \quad \text{on Ag and Cu surfaces.} \qquad (2)$$

In the photocatalytic reaction, electrons produced by photoirradiation can enhance the dissociation of N_2O through electron capture (reaction (3)). The surface is refreshed by the elimination of adsorbed oxygen species by reaction (4).

$$N_2O + e^- \rightarrow N_2 + O^-_{(ad)} \qquad (3)$$

$$O^-_{(ad)} + H^+ + e^- \rightarrow OH^- \qquad (4)$$

On the other hand, CH_3OH is oxidized by holes on TiO_2 surfaces. The photocatalytic reduction of N_2O efficiently proceeded on the Ag- and Cu-supported TiO_2 powder through such a mechanism in which the dissociation absorption of N_2O on the Ag and Cu surfaces was involved.

Acknowledgement

The authors gratefully acknowledge the financial support from the First Toyota High-tech Research Grant Program and Mitsubishi Petrochemical Co. This work was also supported by a Grant-in-Aid (No. 09640696) from the Ministry of Education, Science, Sports, and Culture, Japan.

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