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NOTE

Rare Earth Ions as Heterogeneous Photocatalysts for the Decomposition of Dinitrogen Monoxide (N_2O)

Optical and spectroscopic properties of rare earth ions have been extensively investigated (1–7). Generally, the photoexcited state of the rare earth cations is generated by the absorption of light, corresponding to the transition of the electrons situated in the inner $4f$ orbital to the $5d$ orbitals ($4f$–$5d$ transition) or to other $4f$ orbitals (f–f transition) (2–7). The ions in the excited state have the capability of transfering their excited energy to other molecules in the gas phase or in the adsorbed state (8). Such energy transfer processes can lead to the rare earth cations acting as photocatalysts. However, little has been reported about their photocatalysis, except for the photochemical evolution of hydrogen (9, 10) and the photochemical conversion of α-methylstyrene to 2,3-dimethyl-2,3-diphenylbutane and 3,4-dimethyl-3,4-diphenylpentanol using europium chlorides in a homogeneous liquid phase (11).

In the present note, the authors report evidence for the heterogeneous photocatalysis of rare earth cations in the decomposition of dinitrogen monoxide (N_2O) into nitrogen and oxygen molecules. The authors found that praseodymium (Pr) ion-exchanged mordenite and alumina- and silica–alumina-supported Pr are effective photocatalysts for the decomposition of N_2O. The stoichiometric photodecomposition of N_2O proceeded only on the Pr–mordenite.

Reaction of N_2O (1.05 kPa) with argon diluent at a total pressure of 7.50 kPa was carried out at 286 K in a conventional closed gas-circulating system (187.5 cm^3), in which a quartz-made reactor with a bottom made of a flat, transparent quartz window was installed. The photocatalyst sample was degassed under a vacuum of $<10^{-4}$ Torr (1 Torr = 133.3 Pa) at 873 K prior to being used in the reaction. The light from a medium-pressure-type mercury lamp (H-400P, Toshiba Co., Ltd.) was irradiated to the catalyst through a water filter. The products, nitrogen and oxygen, were analyzed by gas chromatography.

Lanthanoid ion-exchanged zeolites were prepared by ion exchange of Na-form zeolites (ca. 800 mg) in an aqueous solution of lanthanoid chloride (60 mM, pH 4), followed by washing with deionized water and drying at 383 K, and were calcined at 723 K for 3 h. The Na–mordenite (Na–M) was synthesized by the hydrothermal treatment of aluminosilicate gel (Si : Al = 10). The Na–Y zeolite (Na–Y) was supplied by Tosoh Co., Ltd. The Si : Al ratios of Na–Y and Na–M were 2.3 and 7.8, respectively. The content of praseodymium in the Pr—mordenite (Pr—M) was 1.84 wt%, corresponding to an exchange degree of 27% based on Al content. For the Pr–Y zeolite (Pr–Y), the praseodymium content was 2.67 wt% (exchange degree, 16%). The content of praseodymium in the catalysts was determined by inductively coupled plasma (ICP) emission and the state of the ion in the catalyst was examined using X-ray photoelectron spectroscopy (XPS).

Table 1 summarizes the results of the photodecomposition of N_2O on Pr ion-exchanged zeolites, Pr-supported catalysts, and Pr_6O_{11}. The results on the lanthanoid cation (La, Sm, Eu, and Gd)-exchanged mordenites are also summarized in Table 1. The effectiveness of the catalysts has been evaluated on the basis of the N_2 formation rate, which was determined from the amount of N_2 averaged for the reaction time of the initial 110 min during the photoirradiation of the catalyst. The reaction did not proceed in the dark for the catalysts tested. Pr works efficiently as a photocatalyst for the decomposition of N_2O with Al_2O_3, SiO_2–Al_2O_3, and mordenite supports. Other lanthanoid cation (La, Sm, Eu, and Gd)-exchanged mordenites (Ln–M) exhibited activity in the photodecomposition of N_2O. These were, however, inferior to Pr—M in activity, and the $N_2 : O_2$ ratios of the products were rather far from the stoichiometric value ($N_2 : O_2 = 2$) of the N_2O decomposition. Among the catalysts tested, Pr—M was effective and is a preferred photocatalyst since it evolves N_2 and O_2 in a $N_2 : O_2$ ratio close to the stoichiometric value.

Typical results from the decomposition of N_2O on Pr—M degassed at 873 K are shown in Fig. 1. During the reaction in the dark, little nitrogen was formed. When Pr—M was irradiated with the light from the Hg lamp, the formation of N_2 and O_2 began immediately and increased almost linearly with irradiation time or with the constant rate of the N_2O decomposition. As soon as the irradiation ceased, the formation of N_2 and O_2 stopped. The decomposition rate was reproduced when Pr—M was reirradiated. Therefore, Pr ions in the zeolite are responsible for the photoinduced decomposition of N_2O. The amount of N_2 formed after 370 min was about five times larger than the amount of Pr ion included in Pr—M, indicating that the

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TABLE 1

Results of Photocatalytic Decomposition of N_2O on Various Praseodymium Catalysts and Lanthanoid Cation-Exchanged Mordenites

Catalyst	N_2 formation rate (μmol · min^{-1})	$N_2:O_2$ ratio	Total turnover for *Ln* ion[a]
Pr–Y zeolite[b]	0.0075	2.3	0.3
Pr–mordenite[c]	0.1173	2.1	5.0
La–mordenite[d]	0.0128	3.3	0.5
Sm–mordenite[d]	0.0135	2.8	0.6
Eu–mordenite[d]	0.1059	2.6	4.6
Gd–mordenite[d]	0.0230	2.8	1.0
Na–mordenite	0.0147	3.1	—
Pr/Al_2O_3[e,f,g]	0.0585	2.8	0.5
Pr/Al_2O_3[e,g,h]	0.0582	2.8	2.5
Pr/SiO_2–Al_2O_3[e,f,i]	0.0486	2.5	0.4
Pr/SiO_2–Al_2O_3[e,f,j]	0.0327	2.5	0.3
Pr/SiO_2[e,f,k]	0.0021	12.0	0.02
Pr_6O_{11}[l]	0.0189	3.9	0.02

Note. Reaction conditions: Catalyst weight, ca. 30 mg; reaction temperature, 286 K. Catalyst was degassed at 873 K for an hour prior to the reaction.

[a] Determined for a reaction time of 110 min by the amount of N_2 formation.

[b] Si/Al = 2.2, Pr = 2.67 wt%.

[c] Si/Al = 7.5, Pr = 1.84 wt%.

[d] Si/Al = 7.5, *Ln* ion-exchanged degree = 20–30%.

[e] Prepared by the impregnation of the support in aqueous solution of praseodymium chloride (ca. 60 m*M*), followed by drying at 383 K and calcining at 723 K.

[f] Pr = 8.6 wt%.

[g] Al_2O_3: JRC-ALO-4.

[h] Pr = 1.84 wt%.

[i] SiO_2–Al_2O_3: JRC-SAH-1 (Si/Al = 1.8).

[j] SiO_2–Al_2O_3: JRC-SAL-1 (Si/Al = 4.6).

[k] SiO_2: Kieselgel 100.

[l] Purchased from WAKO Pure Chemical Industries, Ltd. Pr = 82.7 wt%.

photoinduced decomposition of N_2O on Pr—M occurs catalytically. The $N_2:O_2$ ratio in the product of the photocatalytic decomposition on Pr—M was almost 2 : 1, stoichiometrically more ideal than that observed (which was far from 2 : 1) on the copper ion-exchanged ZSM-5 zeolite (12) and on MgO (13).

No remarkable difference in the rates of photocatalytic decomposition of N_2O was observed for Pr–M samples prepared from $PrCl_3$, $Pr(NO_3)_3$ (exchange degree, 20%), and $Pr(CH_3COO)_3$ (exchange degree, 21%) and used as starting materials for the ion exchange of the parent Na–mordenite. Thus, it is concluded that the presence of the Pr cation is essential for the photocatalytic decomposition of N_2O.

When irradiated light of wavelengths less than 250 nm was cut off by a color filter, the N_2O decomposition was completely suppressed, as shown in Fig. 1. The diffuse reflectance spectrum (DRS) of Pr–M degassed at 873 K showed a strong absorption band at around 240 nm and broad bands at around 420–600 nm, for the reference of Na–M, as shown in Fig. 2. The absorption band at 240 nm is assigned to the *f–f* transition ($^3H_4$ level to $^1S_0$ level) or 4*f*–5*d* transition of the Pr^{3+} ($4f^2$) cation (14). The rate of the photocatalytic decomposition of N_2O on Pr–M was proportional to the intensity of the irradiated light at around 240 nm. These results show that the decomposition of N_2O on Pr–M is indeed a photochemical process resulting from the absorption of a photon by a Pr cation in the mordenite. N_2O exhibits no absorption band at around 240 nm. Thus, it is proposed that the transfer of energy from the excited state of the Pr cations to N_2O molecules causes the photosensitized decomposition of N_2O into N_2 and O_2.

The photocatalytic decomposition of N_2O on Pr–M degassed at 873 K was completely suppressed by the water preliminary adsorbed at 303 K. Recovery of the photocatalytic activity to its original value was accomplished by degassing the water-adsorbed Pr–M at 873 K. The adsorption of water on Pr–M caused complete disappearance of the adsorption at 240 nm in DRS, which was recovered by degassing the water-adsorbed Pr–M at 873 K. It is assumed that the coordination of water to the Pr cations reduces the absorption of light by the Pr cations and retards the access of N_2O molecules to the photoactive species (Pr cations).

In situ XPS applied to Pr–M degassed at 873 K showed that the spectrum due to the Pr 3*d* electrons was close to that observed for Pr_2O_3 but different from that for Pr_6O_{11}.

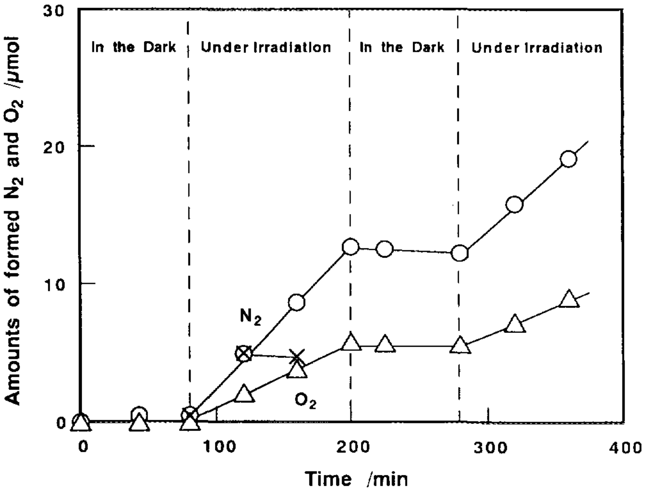

FIG. 1. Change in amounts of N_2 and O_2 during the decomposition of N_2O on the degassed praseodymium ion-exchanged mordenite (30 mg). Cross marks, amount of N_2 with a color filter. The catalyst was irradiated through a color filter for 120 min.

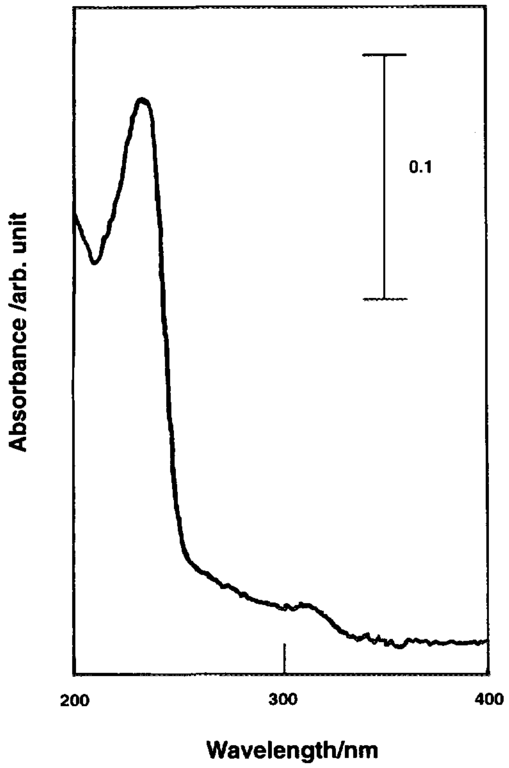

FIG. 2. Diffuse reflectance spectrum of the Pr–mordenite degassed at 873 K. The sodium form of the mordenite was used as a reference material for the measurement.

This result indicates that Pr ions in Pr–M are in the 3+ oxidation state (15), corresponding to the results of the DRS measurements. It is further suggested that the coordination sphere of the Pr^{3+} ions in Pr–M resembles that in Pr_2O_3 constructed with Pr^{3+} surrounded by oxygen anions, but the X-ray diffraction measurement of Pr–M did not show any diffraction pattern of Pr oxides. It is plausible that the Pr ions in Pr–M are surrounded by zeolitic oxygen anions and located on the cation-exchange sites in the cavities as trivalent cations.

The stoichiometric photodecomposition of N_2O occurred only on Pr–M. The amount of oxygen evolved from *Ln*–M (*Ln* = La, Sm, Eu, and Gd) or was less than stoichiometric. Such lower stoichiometric evolution of oxygen on the *Ln*–M must be related to oxygen having a stronger affinity for lanthanoid cations than for Pr cations. While the exchange of isotopic oxygen in the lanthanoid oxide seems to be a measure of the affinity of oxygen for the cations, it is interesting that the praseodymium oxide has the highest activity in the exchange of isotopic oxygen with molecular oxygen (16), ascribed to the ease of $Pr^{3+} \rightleftharpoons Pr^{4+}$ interconversion and, in consequence, to the high oxygen mobility (17).

It is interesting to note that the remarkable activities in the photodecomposition of N_2O were observed on the Pr/Al_2O_3 and Pr/SiO_2–Al_2O_3 catalysts, where the Pr cations are expected to be in the highly dispersed oxide form, because these two catalysts did not show a diffraction pattern of Pr oxides in the X-ray diffraction measurements. It is suggested that the praseodymium cations with a coordination sphere with oxygen ions similar to that for the oxide in Pr_2O_3 must play an important role in photocatalysis by praseodymium cation-exchanged mordenite. The active state of the Pr cation for the photocatalytic decomposition of N_2O is still a matter for further investigation and will be discussed elsewhere.

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