Photocatalytic Decomposition of Acetaldehyde under Visible Light Irradiation over La^{3+} and N Co-doped TiO_2

Yoshiaki Sakatani,[†,††] Jun Nunoshige,[††] Hiroyuki Ando,[†] Kensen Okusako,[†] Hironobu Koike,[†] Tsuyoshi Takata,[††]
Junko N. Kondo,[††] Michikazu Hara,[††] and Kazunari Domen[††]
[†]*Basic Chemicals Research Laboratory, Sumitomo Chemical Co., LTD., 5-1 Sobiraki-cho, Niihama, 792-8521*
[††]*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503*

(Received August 18, 2003; CL-030762)

La^{3+} and N co-doped TiO_2, which contained paramagnetic N species, decomposed acetaldehyde under visible light irradiation. The number of the paramagnetic N species seemed to control the absorption of visible light and the activity.

TiO_2 is the most widely used photocatalyst for the decomposition of various organic pollutants because of its high activity and chemical stability. While the band gap energy of TiO_2 (3.0–3.2 eV) requires UV light irradiation to exhibit the photocatalytic activity, commercial lamps that used in an indoor space mainly emit visible light. Therefore, visible light-responsive photocatalysts have been demanded.

N-doped TiO_2 was found as a visible light-responsive photocatalyst.[1,2] We previously reported that metal ion (M: K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Nb^{5+}, Fe^{3+}, Zn^{2+}, and Al^{3+}) and N were co-doped into TiO_2 powders through polymerized complex (PC) method.[3] Among them, Sr^{2+} and N co-doped TiO_2, which was prepared by PC method, showed the highest photocatalytic activity for decomposition of acetaldehyde under visible light irradiation. It was considered that PC method provided uniform Sr^{2+} doping in the TiO_2 lattice. The uniformity of Sr^{2+} in TiO_2 lattice results in favorable doping of N into TiO_2 without forming Ti^{3+} and lattice defects.

La^{3+} and N co-doped TiO_2 (La–N–TiO_2) powders were prepared in this study by PC method.[3,4] Titanium tetraisopropoxide (TIPO, Kanto Chemical; 97%) was dissolved into a mixture of ethylene glycol (EG, Kanto Chemical; 99.5%) and methanol (Kanto Chemical; 99.8%), and then lanthanum nitrate (Kanto Chemical; 99.5%), and citric acid (CA, Wako Pure Chemical; 98%) were added to this solution. The molar ratio of TIPO: CA:EG:La was fixed at 100:501:1754:0 or 0.5. The solution was heated by using a hot stirrer to promote polymerization of TIPO and CA, and excess methanol was removed. After continuous heating for a few hours, the solution became highly viscous, and transparent brown resin was finally obtained. The resin was calcined at 923 K for 4 h in air to provide white precursor oxide powder. The precursor oxide powder was calcined in NH_3 flow at 773 K for 10 h to obtain La–N–TiO_2 powder. Hereafter, 0.5 mol % La^{3+} doped La–N–TiO_2 is referred to as "La0.5–N–TiO_2," whereas N doped powder (without doping La^{3+}) is designated as "N–TiO_2."

Various properties of N–TiO_2, La0.5–N–TiO_2, and N-doped TiO_2 (N–ST-01) are summarized in Table 1. N–ST-01 was obtained by nitriding ST-01 (Ishihara) under NH_3 flow at 773 K for 3 h. N–TiO_2 had gray color due to the presence of Ti^{3+} in the TiO_2 lattice. Furthermore, an ESR signal attributed to lattice defects was observed in N–TiO_2. On the other hand, La0.5–N–TiO_2 and N–ST-01 had yellow color. BET surface area of N–TiO_2 was smaller by about an order of magnitude than that of La0.5–N–TiO_2. Crystal structures of N–TiO_2 and La0.5–N–TiO_2 were rutile and anatase, respectively. The doped La^{3+} suppressed the generation of Ti^{3+} and lattice defects in the TiO_2 lattice as well as the crystalline growth. The N content in N–ST-01 was the largest in the samples.[5] It seems that the N content was proportional to the surface area. The large surface area facilitated the N doping into the TiO_2 lattice under NH_3 flow.

Photodecomposition of acetaldehyde into CO_2 was used to evaluate the photocatalytic activity. Photocatalyst (0.3 g) was placed in a sealed-type glass reaction vessel (volume: 0.5 L). A mixture of oxygen and nitrogen (1:4) containing 600 ppm of gaseous acetaldehyde filled the reaction vessel. Then, visible light (450–830 nm) irradiated outside of the vessel. A 500-W xenon lamp equipped with a UV and an infrared cut-off filters was used as a light source. The generated CO_2 concentration was measured by a photo-acoustic multi gas monitor (type: 1312; INNOVA). As apparent in Table 1, La0.5–N–TiO_2 exhibited much higher activity than the other samples. The presence of Ti^{3+} and the lattice defect in the TiO_2 lattice together with the small surface area resulted in the low activity of N–TiO_2. Despite of the large surface area, N–ST-01 showed the low activity due to the weaker absorption in the visible region than La0.5–N–TiO_2 (Inset in Figure 1).

Figure 1 shows the dependence of CO_2 evolution rate by decomposition of acetaldehyde under visible light irradiation over La0.5–N–TiO_2 upon the irradiated wavelength controlled by using various cut-off filters. The light with wavelength lower than 500 nm was available for the decomposition of acetaldehyde over La0.5–N–TiO_2. 1200 ppm CO_2 was evolved when 600 ppm acetaldehyde reacted under visible light (450–830 nm) irradiation, which indicates that La0.5–N–TiO_2 could decompose acetaldehyde completely. As shown in Figure 1, the activity by irradiating UV light stayed at the same level as that of P-25 (Degussa); however, P-25 showed no activity under

Table 1. Various properties of N–TiO_2, La0.5–N–TiO_2, and N–ST-01

	Color	BET surface area / m^2/g	Crystal structure	N content /atm%	Rate of CO_2 evolution / ppm/h
N–TiO_2	Gray	6	Rutile	0.45	7
La0.5–N–TiO_2	Yellow	48	Anatase	1.02	118
N–ST-01	Yellow	126	Anatase	2.30	34

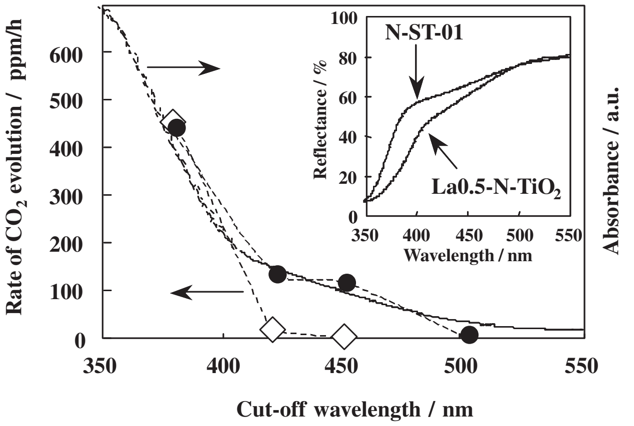

Figure 1. CO_2 evolution rates by photocatalytic decomposition of acetaldehyde over La0.5–N–TiO_2 (●) and P-25 (◇), and UV–vis diffuse reflectance spectrum of La0.5–N–TiO_2 as a function of the cut-off wavelength for irradiation. Inset shows reflectance spectra of La0.5–N–TiO_2 and N–ST-01.

visible light irradiation. Figure 1 also shows UV–vis diffuse reflectance spectrum over La0.5–N–TiO_2. The absorption feature of La0.5–N–TiO_2 well agreed with the activity.

Figure 2 shows ESR spectrum of La0.5–N–TiO_2 under visible light (450–800 nm) irradiation in evacuation condition at 77 K, where a triplet signal was observed. Ti^{3+} ($g = 1.96$) signal was not detected. The visible light irradiation was carried out by using 500-W xenon lamp equipped with the ultraviolet and the infrared cut-off filters. It was also reported that the triplet signal was attributed to paramagnetic N species (e.g. NO, NO_2, NO^{2-}, $NO_2{}^{2-}$) existing in TiO_2.[6,7] It is considered that NH_3 was doped into the precursor oxide under NH_3 calcination, and that the doped NH_3 was reacted with lattice oxygen to form the paramagnetic N species. The triplet signal was also observed in dark condition, and what is more, the intensity of the triplet signal was increased by visible light irradiation as well as UV irradiation.

The increase in intensity indicates the generation of the paramagnetic N species even by visible light irradiation. The number of the paramagnetic N species was roughly estimated by spin concentration at the main peak ($g = 2.002$–2.008) of the triplet signal.[8] Figure 3 shows the spin concentration over La0.5–N–TiO_2 against irradiated cut-off wavelength, and the spin concentration became larger with decreasing wavelength. The behavior of the spin concentration in visible light region was similar to that of the activity as well as the absorption spectrum as shown in Figure 1. The reaction mechanism of the N-doped TiO_2 was suggested that the substitution of N at O site in TiO_2 lattice forms Ti–N bond and enables to decrease the band gap energy and to provide the photocatalytic activity under visible light irradiation. However, La0.5–N–TiO_2 did not have N 1 s peak at 396 eV (Ti–N bond).[9] The doped N did not exist at O site in TiO_2 lattice. From these results, we anticipate that the number of the spin concentration is responsible to absorb visible light and to exhibit the activity under visible light irradiation. The activity under visible light irradiation would be given by the photo-excitation at active sites related to the paramagnetic N species. On the other hand, the spin concentration under UV light irradiation, "No filter" in Figure 3, was not very high in comparison with that under visible light irradiation. The activity under UV light irradiation is considered to be provided by band gap excitation in TiO_2. The detailed mechanism of the visible light response has not been clear yet, further study is necessary.

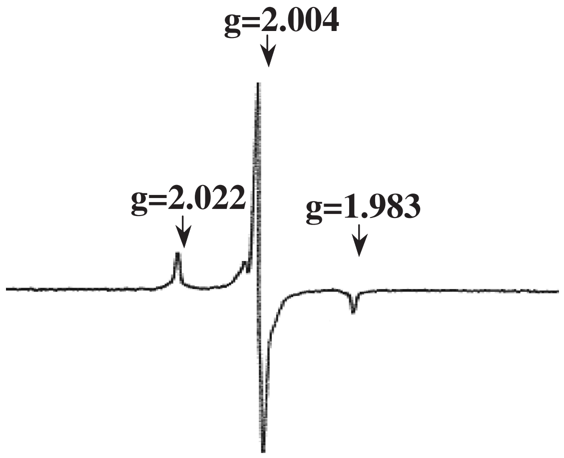

Figure 2. ESR spectrum of La0.5–N–TiO_2 under visible light (450–800 nm) irradiation in evacuation condition at 77 K.

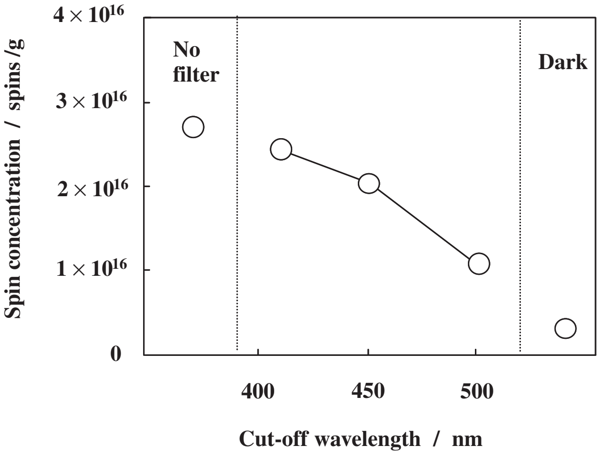

Figure 3. Spin concentration at the main peak ($g = 2.002$–2.008) of the triplet signal as shown in Figure 2 as a function of the cut-off wavelength for irradiation.

In summary, La–N–TiO_2 was obtained by calcining the La^{3+} doped precursor oxide under NH_3 flow. The doped La^{3+} hindered the formation of Ti^{3+} and the lattice defect and the crystal growth. The number of the paramagnetic N species seemed to control the absorption of visible light and the activity under visible light irradiation.

References and Notes

1 S. Sato, *Chem. Phys. Lett.*, **123**, 126 (1986).
2 R. Asahi, T. Morikawa, T. Ohwaki, and Y. Taga, *Science*, **293**, 269 (2001).
3 Y. Sakatani, J. Nunoshige, H. Ando, K. Okusako, H. Koike, T. Takata, J. N. Kondo, M. Hara, and K. Domen, submitted to.
4 M. Kakihana, *J. Sol-Gel Sci.*, **5**, 7 (1996).
5 The nitrogen content was measured by using a nitrogen analyzer (EMGA-2800; Horiba Ltd.)
6 M. Che and C. Naccache, *Chem. Phys. Lett.*, **8**, 45 (1971).
7 R. D. Iyengar and R. Kellerman, *J. Colloid Interface Sci.*, **35**, 424 (1971).
8 The spin concentration was estimated by using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) as a standard substance.
9 Y. Sakatani, J. Nunoshige, H. Ando, K. Okusako, H. Koike, T. Takata, J. N. Kondo, M. Hara, and K. Domen, in preparation.

Published on the web (Advance View) November 17, 2003; DOI 10.1246/cl.2003.1156