Effect of transition metal elements addition on the properties of nitrogen-doped TiO2 photocatalysts

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Received 22 October, 2011, Revised 26 November, 2011

Abstract. Nitrogen-doped TiO2 (TiO2-xNy) nanoparticles with and without adding the transition metal ions, such as Co2+ and Ni2+, were synthesized by thermohydrolysis of TiCl3. The samples were characterized by X-ray diffraction, specific surface area determination, UV-vis diffuse reflectance spectroscopy. The photocatalytic activity of the sample was investigated by employing the oxidative destruction of nitric oxide as a probe reaction using a continuously flowing gases-solid system. Although the doping of transition metal ion in the lattice of titania was not useful to improve the photocatalytic activity, loading of transition metal oxides on the surface of titania resulted in an improvement of the photoreactivity of the nitrogen-doped TiO2. The beneficial effect was explained by an increased separation efficiency of the photogenerated electron-hole pairs.

1. Introduction
Titanium dioxide is the most-used photocatalyst because of the facile synthesis, stability under various reactions media, cheapness, and bands position compatible with the oxidation of many organic compounds [1,2]. However, because of its large band gap (3.2 eV), TiO2 can be only excited by UV light irradiation of less than the wavelength of 400 nm. Several studies have been carried out with the aim to extend the optical response to the visible-light region and to slow down the recombination rate of the electron-hole pairs by selective doping of TiO2 with metal ions [3-5] or with non-metal anionic species [6-8]. Many controversial results are reported in literature because the method of doping strongly determines the properties of the resulting catalysts.

The most important advance in this field should be attributed to the nitrogen doped TiO2, which was first reported by Asahi et al. in 2001 [9,10]. By doping with nitrogen ion from N2 or NH3 atmosphere or other nitrogenous organics, the band gap of titania could be narrowed since the valence band of N2p band locates above O2p band. While, besides anion doping, studies on transition metal ion doping have also proven to be an efficient method to improve the photocatalytic properties of TiO2. Among them, Fe, Co, and Ni were suggested as one of the most promising candidates due to its effect in depressing electron-hole recombination rate and shifting the absorption onset to visible-light region [11-16]. In a previous paper [12], it was reported that the Fe and N co-doping titania, Ti1-xFeO2-2yNz,
caused the decrease in photocatalytic activity, due to the formation of lattice vacancy, but TiO$_2$-$x$N$_y$/Fe$_2$O$_3$ composites showed excellent photocatalytic activity, due to the heterogeneous electron transfer from TiO$_2$-$x$N$_y$ to Fe$_2$O$_3$ to retard the quick recombination of photoinduced electrons and holes.

In this work, nitrogen-doped titania added transition metal ion, such as Co$^{2+}$ and Ni$^{2+}$ were prepared by two different hydrothermal methods to clarify the effect of transition metal ion addition on the photocatalytic activity.

2. Experimental

2.1. Preparation of photocatalysts

Co$^{2+}$ or Ni$^{2+}$ contained TiO$_2$-$x$N$_y$ was prepared by the similar hydrothermal method reported in a previous paper [12,17,24]. 20 wt.% of TiCl$_3$ aqueous solution and hexamethylenetetramine (HMT) were used as the titanium and nitrogen source, respectively. CoCl$_2$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O were used as Co$^{2+}$ or Ni$^{2+}$ sources. These ions were added to TiO$_2$-$x$N$_y$ by two different methods, such as the 1-step reaction and 2-step reaction. 1-step reaction: after dissolving all starting materials, the solution was heated at 190ºC for 15 min by a microwave oven. 2-step reaction: After fabricating TiO$_2$-$x$N$_y$ nanoparticles by the microwave assisted hydrothermal reaction of TiCl$_3$ and HMT, the transition metal salt was added in the solution, followed by a hydrothermal reaction at 190ºC for 15 min by a microwave oven. Finally, the samples were vacuum dried at 60ºC overnight. The amount of transition metal ions in the final products was changed in the range from 1 to 10 mol.%

2.2. Characterization

The chemical compositions of the samples were determined by the EDX spectrometer (Rayny EDX-800HS, Shimadzu). The crystalline phases of the samples were determined with X-ray diffraction analysis (XRD, Shimadzu XD-D1). The morphology of the samples was observed by TEM (JEOL, JEM-2010). BET measurements (Quantachrome Instruments, NOVA 4200e) were performed to determine the specific surface areas. The ultraviolet-visible diffuse reflectance spectrum was taken by a UV-vis spectrophotometer (Shimadzu, UV-2450).

2.3. Photocatalytic reaction

To evaluate the photocatalytic activities of the prepared samples, the oxidative decomposition behaviour of NO gas was investigated using a flow type reactor under irradiation of a 450 W high pressure mercury arc at room temperature. The detailed experimental apparatus used for the photocatalytic reaction was reported in a previous paper [18]. During the experiment, a 2 ppm standard NO gas (balance N$_2$) was mixed with air (1:1), and passed through the reactor (373 cm$^3$ of internal volume) continuously throughout the reaction. The sample was placed in the hollow (20 mm×16mm×0.5 mm) of a glass holder plate and set in the bottom center of the reactor. To reach the adsorption and desorption equilibrium, the sample was allowed to contact with the NO gas for more than 10 min. After that, the light was turned on to start the photocatalytic reaction. The mercury arc was put 165 mm away from the reactor, and it was cooled by using a Pyrex jacket with cooling water at 30 ºC during the irradiation. Furthermore, an electric fan was also used to cool the reaction system. The wavelength of the irradiation light was controlled using several filters: Pyrex glass for $>$ 290 nm, Kenko L41 Super Pro (W) filter $>$ 400 nm and Fuji triacetyl cellulose filter $>$510 nm. The evaluation time for one sample under the irradiation with each wavelength was 10 min. The concentration of NO was determined using a NO$_x$ analyzer (Yanaco, ECL-88A). It has been reported that during the photocatalytic decomposition, about 20 % of NO is directly reduced to N$_2$ and the other 80 % is oxidized to NO$_3^-$ species [19].

3. Results and discussion
Table 1. EDX analysis results of the transition metal – nitrogen co-doped TiO$_2$ synthesis by 1-step and 2-step methods.

| Added amount /mol.% | Co / mol.% | Ni / mol.% |
|---------------------|------------|------------|
|                     | 1-Step     | 2-Step     | 1-Step | 2-Step |
| 1                   | 1.2        | 1.1        | 0.9    | 1.3    |
| 3                   | 3.2        | 2.8        | 3.1    | 3.3    |
| 5                   | 4.2        | 4.1        | 4.3    | 4.1    |
| 19                  | 9.4        | 9.1        | 8.5    | 8.7    |

The Co$^{2+}$ and Ni$^{2+}$ contents in the prepared samples are shown in Table 1. The results suggest that Co$^{2+}$ or Ni$^{2+}$ added were almost completely incorporated in the sample by both 1-step and 2-step reactions.

Figure 1. XRD patterns of the samples prepared by (A) 1-step method and (B) 2-step method with different Co$^{2+}$ and Ni$^{2+}$ contents.
Figure 2. TEM images of (a) TiO$_{2}$N$_{y}$, and that added 10 mol.% of (b) Co and (c) Ni by (a1,b1,c1) 1-step and (a2,b2,c2) 2-step method.

The XRD patterns of the samples prepared by two different ways are shown in Fig. 1. No XRD peaks corresponding to the cobalt and nickel compounds appeared, even in the case of 10 mol.% Co$^{2+}$ and Ni$^{2+}$ addition. The reason might be explained as these transition metal ions were doped into the TiO$_{2}$ lattice and/or the very fine dispersions of transition metal oxide were formed on the surface of the titania, resulting in X-ray amorphous behaviour [11-16, 20]. All samples showed very broad diffraction peaks, indicating small crystallite sizes. All of Co$^{2+}$ added samples consisted of the mixed
phases of anatase and rutile. In contrast, 10 mol.% Ni$^{2+}$ added sample by the 1-step method mainly consisted of anatase phase, while the peak intensity of rutile increased with the decrease in Ni$^{2+}$ content, indicating the depression of the formation of rutile by Ni$^{2+}$. However, 10 mol.% Ni$^{2+}$ added sample by the 2-step method consisted of the mixed phases of anatase and rutile. This indicates that the phase transformation of metastable anatase to a thermodynamically stable rutile proceeded, since the hydrothermal treatment was conducted twice in 2-step method. The samples with mixed crystalline phases were expected to show superior photocatalytic activities to single phase samples, since the effective charge separation by the heterogeneous electron transfer can be expected as P25 TiO$_2$ [21,22].

The morphology of the sample was observed by TEM, and the images are shown in Fig. 2. It is observed that the TiO$_{2-x}$N$_y$ consisted of mainly rod-like nanoparticles with the diameter below 10 nm and the length about 20 nm. The samples prepared by the 1-step method showed very similar morphology to that of TiO$_{2-x}$N$_y$ without doping modification, indicating that transition metal doping did not show any influence on the morphology. The samples prepared by the 2-step method showed larger rod-like particles, probably due to the Ostwald ripening under repeated hydrothermal treatment. Compared with the particle size of Fe$^{3+}$ added TiO$_{2-x}$N$_y$ samples (range from 20 to 60 nm) prepared by the hydrothermal reaction using an electric oven in a previous work [12], Co$^{2+}$ and Ni$^{2+}$ added TiO$_{2-x}$N$_y$ prepared in the present study showed much smaller particle size. The smaller particle size might be attributed to the quick microwave-assisted hydrothermal reaction used in the present study.

The specific surface areas of the samples are summarized in Fig. 3. The specific surface areas of Fe$^{3+}$ added samples fabricated using an electric oven were ca. 165 m$^2$/g [12], while those of Co$^{2+}$ and Ni$^{2+}$ added samples using a microwave oven were much higher as ca. 250-400 m$^2$/g. The values of 2-step samples were slightly smaller than those of 1-step samples, due to the crystal growth by twice hydrothermal reaction. It is also notable that the specific surface area did not change so much by adding Co$^{2+}$, but decreased by adding Ni$^{2+}$, indicating the promotion of the crystal growth in the presence of Ni$^{2+}$.

The diffuse reflectance spectra of Co$^{2+}$ and Ni$^{2+}$ added samples are shown in Fig. 4. By adding Co$^{2+}$ and Ni$^{2+}$ to TiO$_{2-x}$N$_y$, the visible-light absorption ability increased, especially above 500 nm of wavelength. For the samples prepared by the 1-step method, the enhancement in visible-light absorption by Co or Ni co-doping might be attributed to the formation of extra bands below the conduction band by mixing Ti 3d and Co or Ni 3d orbitals [11-16]. On the other hand, for the samples prepared by the 2-step method, the coupling of transition metal oxides with TiO$_{2-x}$N$_y$ effectively increased the visible light absorption in Fig. 5(C, D).
Figure 4. Diffuse reflectance spectra of TiO$_{2-x}$N$_x$, and the samples prepared by (A-B) 1-step method or (C-D) 2-step method with different (A,C) Co or (B,D) Ni contents.

The photocatalytic activities for the oxidative decomposition of NO gas are shown in Fig.5. The TiO$_{2-x}$N$_x$ without transition metal ion showed excellent activity even under visible-light irradiation due to the narrowing of band gap energy by N doping. In case of 1-step method, the addition of Co$^{2+}$ resulted in the decrease in the photocatalytic activity, whereas the photocatalytic activity increased by the addition of a small amount of Ni$^{2+}$ less than 5 mol.% and then decreased. The increase in the photocatalytic activity might be due to the increase in the visible-light absorption ability, whereas the decrease in the photocatalytic activity might be due to the promotion of the recombination of photoinduced electrons and holes by the increase in the oxygen vacancy for the charge compensation. Namely, the samples prepared by the 1-step method actually gave a co-doping of transition metal and N in TiO$_2$, in which transition metal ions substituted Ti$^{4+}$ and N$^{3-}$ substituted O$^{2-}$ in the lattice structure. Anion vacancies would be formed in the lattice to maintain the electro-neutrality, which would act as the recombination centers for photo-induced electrons and holes to depress the activity. Bechstein et al. [23] also found the experimental evidence for enhanced surface oxygen vacancy formation upon Cr$^{3+}$ doping of titania. Therefore, the more transition metal ions were co-doped into the products, the poorer the photocatalytic activity of the samples would be, due to the increasing amount of anion vacancy.
Figure 5. Photocatalytic activities for the oxidative decomposition of NO of TiO$_{2-x}$N$_y$, and the samples prepared by 1-step method (A, C), or by 2-step method (B, D), with different Co (A, B) or Ni (C, D) contents.

On the other hand, the photocatalytic activity of Ni$^{2+}$ added sample by the 2-step method increased with an increase of Ni$^{2+}$ content up to 5 mol.% and then was almost constant. In case of the 2-step method, TiO$_{2-x}$N$_y$ particles were first precipitated, followed by the precipitation of NiO particles on the surface of TiO$_{2-x}$N$_y$ particles to form TiO$_{2-x}$N$_y$/NiO composites. Therefore, the increase in the photocatalytic activity in the initial stage may be due to the effective separation of photo-induced electrons and holes by the heterogeneous electron transfer from TiO$_{2-x}$N$_y$ to NiO. Even though the samples prepared by the 2-step method showed lower specific surface areas, they still showed higher photocatalytic activities than those prepared by the 1-step method. Co$^{2+}$ added sample by the 2-step method also showed higher photocatalytic activity than that by the 1-step method, but the enhancement by Co$^{2+}$ addition was modest and the addition of an excess amount of Co$^{2+}$ resulted in the decrease in the photocatalytic activity, although the reason has not been clarified yet.

The photocatalytic behaviours of Ni$^{2+}$ added TiO$_{2-x}$N$_y$ were similar to that of Fe$^{3+}$ added TiO$_{2-x}$N$_y$ reported in a previous paper, but the activity of Ni$^{2+}$ added sample prepared in the present study was higher than Fe$^{3+}$ added samples. The formation of mixed phases of anatase and rutile phase under this 2-step synthesis method could also favor high photocatalytic activity. Furthermore, Ni-modified TiO$_2$ N$_y$ showed optimal photocatalytic deNO$_x$ abilities under both visible-light and UV light irradiation.
4. Conclusion

With the same starting materials, transition metal (Co or Ni) ion-modified TiO$_{2-x}$Ny was synthesized by 1-step and 2-step hydrothermal method. Transition metal ion doping and transition metal oxide loading could be synthesized by these two methods. The photocatalytic activity in NO destruction was decreased by the co-doping of excess amount of transition metal ion, due to the increase in oxygen vacancy. In contrast, the combination of TiO$_{2-x}$Ny with transition metal oxides by the 2-step hydrothermal method showed a positive effect to enhance the photocatalytic activity owing to the effective separation of photo-induced electrons and holes. The current results suggested the importance of element status on the photocatalytic activity, and also provided a clue to design highly active photocatalyst.

Acknowledgments

This research was supported in part by the Management Expenses Grants for National Universities Corporations from the Ministry of Education, Culture, Sports, Science for Technology of Japan (MEXT), and by the Grant-in-Aid for Science Research (No.20360293 & No. 22651022).

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