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Photocatalytic oxidation of NO_x by Pt-modified TiO_2 under visible light irradiation

Yoichi Ishibai [a,*], Junya Sato [a], Shoichi Akita [a], Takashi Nishikawa [a], Shigeyoshi Miyagishi [b]

[a] *Functional Materials R&D Division, Ishihara Sangyo Kaisha, LTD, 1, Ishihara-cho, Yokkaichi, Mie-pref. 510-0842, Japan*
[b] *Graduate School of Natural Science and Technology, Division of Material Science, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa-pref. 920-1192, Japan*

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Abstract

Photooxidation of NO_x has been studied using titanium dioxide (Ishihara ST-01) treated with H_2PtCl_6. The experimental results indicate that Pt-modified TiO_2 with different ligand structures can be synthesized according to the Pt treating procedure. TiO_2 photocatalysts with certain Pt complexes produced significantly high photocatalytic activity under visible light irradiation without decreasing photoactivity under UV light irradiation. The visible-light-induced photocatalytic activity depended on the amount of Pt, but not greatly on the coordination number of Cl ions. It was suggested that the surface complex formation associated with Ti–O–Pt chemisorption dominated the visible light reactivity.
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1. Introduction

Titanium dioxide (TiO_2) is the most promising photocatalyst among the many kinds of metal oxide semiconductors because of its high photocatalytic activity, chemical stability, nontoxicity and commercial availability.

In the past decade, TiO_2 photocatalysts have been widely used in various fields such as self-cleaning coating agents on exterior building materials, photocatalytic paint for removal of nitric oxide on roads, and home-use air purifiers [1]. Unfortunately, the light sources for photocatalytic reactions in these applications are limited to sunlight, which includes only 2–3% ultraviolet, or to artificial ultraviolet lamps corresponding to the band gap energy of TiO_2 (3.2 eV).

Therefore, it is very important practically as well as scientifically to develop a new TiO_2 photocatalyst which works efficiently under visible light. In order to extend the absorption wavelength range into the visible light region, various approaches have been tried. These include doping transition metals into TiO_2 [2,3], covering the surface with dyes [4–6], doping nitrogen into TiO_2 [7–9], and doping sulfur intoTiO_2 [10,11].

Kisch et al. reported that both an amorphous micro-porous titania and an anatase powder with large specific surface area, containing platinum (IV), were able to catalyze the photodegradation of 4-chlorophenol (4-CP) in aqueous solution under visible light irradiation [12–16]. Recently, Zhao et al. found that hexachloro-platinate (IV) anions chemisorbed on TiO_2 enhanced the photodegradation of the azo dye ethyl orange under visible light irradiation [17]. Most of these studies have focused on the reaction mechanism for the photocatalytic degradation of the reactants in aqueous solutions. However, there have been few investigations in which photocatalysts responding to visible light have proved particularly important in practical applications.

In this work, we prepared different Pt-modified TiO_2 samples and compared their photocatalytic activities using a nitrogen oxide (NO_x) gas removal system. The effect of the Pt modifying procedure on the Pt complex structure and on the photocatalytic activity is also discussed.

2. Experimental

2.1. Chemicals

The titanium dioxide powder used as a base photocatalyst was Ishihara ST-01, which is the pure anatase phase. Chloropla-

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* Corresponding author. Tel.: +81 593 45 6116; fax: +81 593 45 6161.
E-mail address: y-ishibai@iskweb.co.jp (Y. Ishibai).

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tinic acid ($H_2PtCl_6{\cdot}6H_2O$) was obtained from Ishihuku Kinzoku Kogyo Co. Inc. and used without further purification. Hypophosphorous acid, formic acid and sodium hydroxide of reagent grade were obtained from Kanto Chemical Co. Inc.

2.2. Preparation of Pt-modified TiO_2

Five kinds of TiO_2 containing Pt were prepared by impregnation, neutralization and reduction methods, using $H_2PtCl_6{\cdot}6H_2O$ and TiO_2 suspension as follows.

2.2.1. Impregnation method (TiO_2(I), TiO_2(I′))

TiO_2 powder (50 g) was dispersed into a 200 ml aqueous solution of 0.34% $H_2PtCl_6{\cdot}6H_2O$ (Pt:TiO_2(w/w) = 0.5:100).

After mixing for 1 h, the suspension was evaporated at 90 °C until dry for TiO_2(I), or was filtered and dried at 105 °C for TiO_2(I′).

2.2.2. Neutralization method (TiO_2(N))

After a TiO_2 dispersion was prepared as above, the suspension was adjusted to pH 7 with 10% NaOH. Then the resulting suspension was aged at 90 °C for 60 min. After aging, Pt-modified TiO_2 was filtered, washed and dried at 105 °C.

2.2.3. Reduction method (TiO_2(P), TiO_2(F))

After a TiO_2 dispersion was prepared as above, 0.30 ml of H_3PO_2 for TiO_2(P) or 0.68 ml of HCOOH for TiO_2(F) was added into the dispersion and the dispersion was aged at 90 °C for 60 min. Then the suspension was adjusted to pH 7 with 10% NaOH. After the neutralization, Pt-modified TiO_2 was filtered, washed and dried at 105 °C.

2.3. Characterization

The particulate morphology of TiO_2 was observed by using a HR-TEM (Hitachi Model H-8100). The crystal structure of the powders was studied on an X-ray diffractometer (Rigaku Model RINT-2200) with Cu Kα radiation. The crystallite size of the powder was estimated from X-ray line broadening. Specific surface areas were determined by the Brunauer–Emmet–Teller method. The diffuse reflective UV–vis spectrum was measured using a Hitachi U-3300 spectrometer equipped with a diffuse reflectance attachment. The composition of the powder was determined using an X-ray fluorescence spectrometer (Rigaku Model RIX-3000). The X-ray photoelectron spectra (XPS) of the powders were measured on a JEOL JPS-100SX spectrometer using Mg Kα as an X-ray source. The binding energy was corrected by taking the C1s level as 284.5 eV.

2.4. Photocatalytic reaction

The photocatalytic activity was evaluated by measuring the oxidation of nitrogen oxide using a continuous-flow type reactor. First, NO was mixed with humidity controlled synthetic air at a concentration of 3 ppm, and then was introduced into the reactor at a flow rate of 3 l/min. A petri dish containing 4.0 g of TiO_2 was placed in a reaction vessel and irradiated with light after it was allowed to stand in the dark for 30 min. Irradiation was performed with a black fluorescent light (Matsushita Electric Model FL20SBL-B) and a white fluorescent light (Toshiba Model FL20SS-W) equipped with a L42 filter (Asahi Techno Glass) to remove light below 420 nm. The illumination intensity at the surface of sample was 3 mW/cm^2 for UV and 5700 lx for visible light. The NO_x concentrations at the inlet and outlet of the reactor were measured every 6 min using a nitrogen oxide analyzer ML9841A (Monitor Labs Inc.) and recorded for 210 min.

For the evaluation of durability of Pt-modified TiO_2, TiO_2 samples after photocatalytic reaction were washed and reinvestigated their photocatalytic activities in the same manner as above. The washing procedure was as follows. TiO_2 powder after photocatalytic reaction was dispersed into 300 ml of water. After stirred for 10 min, TiO_2 was filtered, and the filter cake was washed until electroconductivity of the filtrate was 50 μS/cm. Then, TiO_2 was dried at 105 °C for 30 min.

3. Results and discussion

Five different types of Pt-modified TiO_2 were prepared as photocatalysts. Table 1 shows the physical properties of these samples. Pt contents measured by X-ray fluorescence analysis were in the range of 0.42–0.47%, which agreed with each other within experimental error. The specific surface area was slightly decreased upon Pt modification in all samples. From X-ray diffractometer measurement, all samples were found to be anatase phase. The X-ray diffraction pattern indicated that the samples were nearly the same in crystal characteristics as ST-01. These results indicate that neither crystal transformation nor crystal growth occurred in these Pt modifying processes.

These samples were different in powder color. That is, TiO_2(I), TiO_2(I′), TiO_2(N) and TiO_2(P) were light yellow, while TiO_2(F) was grayish, indicating the presence of Pt(0) due to the reduction of Pt. The diffuse reflectance spectra of TiO_2(I),

Table 1
Physical descriptions of Pt-modified TiO_2 and ST-01

Sample	BET surface area (m^2/g)	Crystallite size (nm)	Powder color	Pt content (wt%)	Cl content (wt%)	Cl/Pt atomic ratio
TiO_2(I)	280	7.5	Yellow	0.461	0.546	6.5
TiO_2(I′)	255	8.3	Yellow	0.468	0.363	4.2
TiO_2(N)	282	7.9	Yellow	0.444	0.179	2.2
TiO_2(P)	272	7.7	Yellow	0.436	0.070	0.9
TiO_2(F)	285	7.7	Gray	0.418	0.005	0.1
ST-01	314	8.0	White	–	–	–

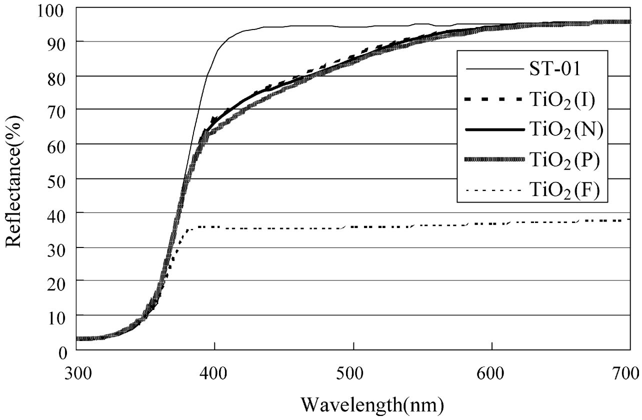

Fig. 1. Diffuse reflectance spectra of Pt-modified samples and ST-01.

TiO_2(N), TiO_2(P), TiO_2(F) and ST-01 are shown in Fig. 1. The base TiO_2(ST-01) had strong absorption only at wavelengths shorter than 400 nm corresponding to its band gap energy, while TiO_2(F) exhibited large absorption over a wide range of visible light. On the other hand, TiO_2(I), TiO_2(N) and TiO_2(P) showed absorption maxima in the short wavelengths region of visible light, corresponding to the yellowish color of the powders. Fig. 2 compares the TEM images of TiO_2(I), TiO_2(N), TiO_2(P) and TiO_2(F). TiO_2 particles with a size below 10 nm are observed in each image. Pt compounds on TiO_2 are too small to be clearly seen in the images of TiO_2(I), TiO_2(N) and TiO_2(P) but Pt particles with the size of 5–10 nm, which seem to be in metallic cluster form were observed only for TiO_2(F). These results indicate that formic acid reduces Pt ion to Pt(0) in the reduction process.

The photocatalytic activity of the samples was evaluated by measuring the photocatalytic oxidation of NO_x ($NO + NO_2$) gases under UV light and visible light irradiation. Fig. 3 shows typical plots of NO, NO_2 and NO_x concentrations in the outlet gas against reaction time in the case of TiO_2(I). In the dark condition after 30 min, the concentration of NO_x became more than 90% of the inlet concentration. Under photoillumination, the concentrations of NO_x greatly decreased at first, and then gradually increased with reaction time. As the initial decrease of NO_x was much greater than the subsequent increase of NO_x, we estimated the initial NO_x removal ratio according to:

$$NO_{x_{\mathrm{removal}}} = \frac{NO_x(\mathrm{d}) - NO_x(\mathrm{l})}{NO_x(\mathrm{d})} \times 100\,(\%) \qquad (1)$$

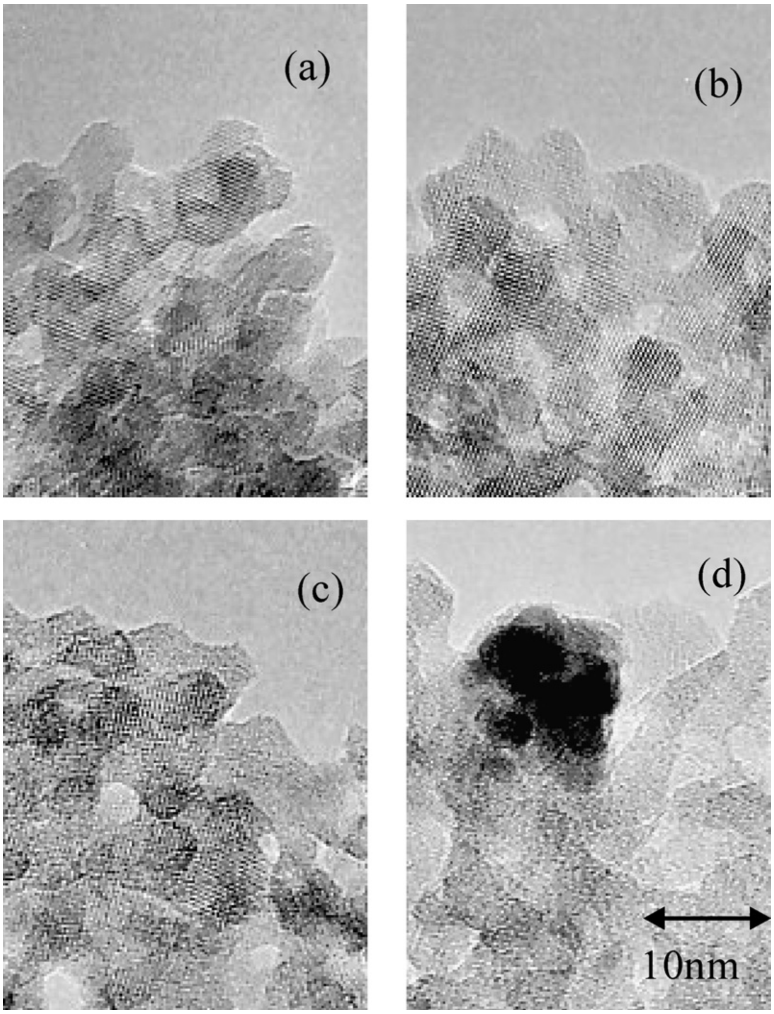

Fig. 2. TEM images of Pt-modified TiO_2. (a) TiO_2(I), (b) TiO_2(N), (c) TiO_2(P) and (d) TiO_2(F).

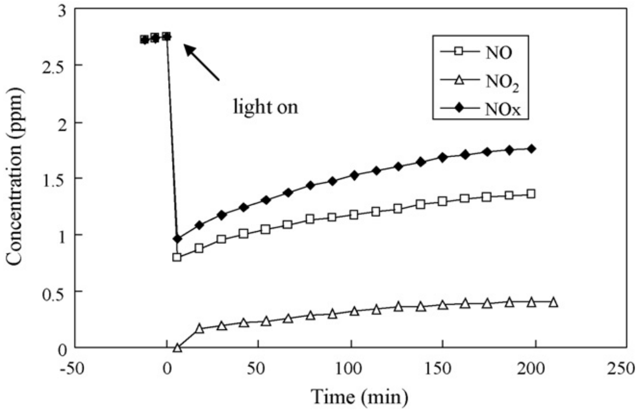

Fig. 3. Typical plots of NO, NO_2 and NO_x concentrations in the outlet gas against reaction time. TiO_2 sample: TiO_2(I); Pt content: 0.5 wt%; light source: white fluorescent light; light intensity: 5700 lx.

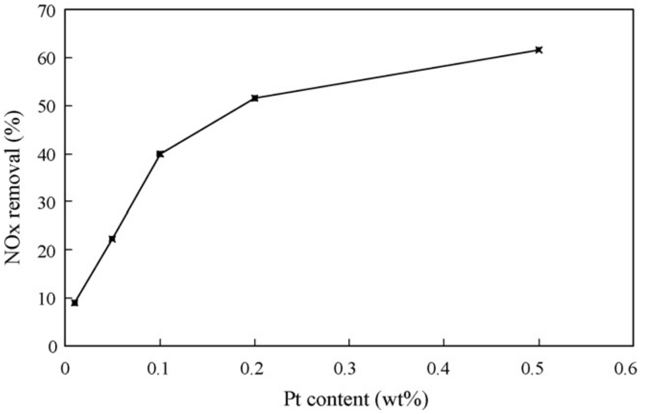

Fig. 4. Influence of Pt content on photocatalytic activity under visible light irradiation. The sample were prepared in neutralization method; TiO_2(N).

where $NO_{x_{\mathrm{removal}}}$ is initial NO_x removal ratio, NO_x(d) and NO_x(l) are the NO_x concentrations under the dark condition and at the time of the maximum decrease after photo irradiation, respectively.

Photocatalytic property under UV light and visible light irradiation is summarized in Table 2. The photocatalytic NO_x removal ratios under UV light irradiation were almost the same for the four Pt-modified TiO_2 samples and were similar to that of base TiO_2 (ST-01). Under visible light irradiation, NO_x was efficiently removed by TiO_2(I), TiO_2(N) and TiO_2(P), and the removal ratio of NO_x was around 60–70%. Meanwhile, only the trace amounts of NO_x were removed in the case of TiO_2(F).

Pt deposition on TiO_2 is well known to enhance photocatalytic activity due to the retardation of electron-hole recombination [18] or due to the formation of a new pathway for the selective oxidation of the reactant [19]. However, metallic Pt deposited on TiO_2 by the redox reaction with formic acid did not enhance the photocatalytic oxidation of NO_x even under UV light irradiation. Lee and Choi reported that the effect of metallic Pt on photocatalytic activity depended on the deposit properties of Pt such as size, amount and oxidation state [20].

The influence of Pt content on the photocatalytic activity under visible light irradiation was investigated with TiO_2(N). As shown in Fig. 4, the initial NO_x removal ratio increased with increasing Pt content up to 0.5%. This indicates that photocatalytic activity strongly depends on the amount of Pt-modified onto a TiO_2 surface.

In the present experimental condition, the concentration of NO_x in the outlet gas increased with reaction time as shown in Fig. 3. The deterioration of photocatalytic activity was evaluated by the ratio of NO_x concentration after visible light irradiation for 210 min (NO_x(l_{210})) to NO_x(l). As summarized in Table 2, each sample showed approximately the same degree of deterioration during the reaction time for 210 min. The decrease of photocatalytic activity is probably due to adsorption of HNO_3 formed by the oxidation of NO_x [21–23]. Ibusuki and Takeuchi [21] showed that photocatalytic activity for NO_x oxidation recovered by washing the used catalyst with purified water in TiO_2-activated carbon catalyst. As an evaluation of durability of Pt-modified TiO_2, we washed TiO_2 samples after photocatalytic reaction and measured their photocatalytic activity. As shown in Table 2, the initial NO_x removal ratio for washed TiO_2(I), TiO_2(N) and TiO_2(P) were found to be 69.1, 57.8, and 66.5, respectively, which are in good agreement with the value obtained for the virgin samples. These results indicated that HNO_3 accumulated on the Pt-modified TiO_2 were removed by washing. Pt-modified TiO_2 in this study, therefore, seemed to have a good stability in water and re-used repeatability in NO_x removal system.

For the further characterization of Pt compounds deposited on TiO_2 particles, the XPS spectrum was measured for the samples produced by different Pt modifying processes. As for the base

Table 2
Photocatalytic properties of Pt-modified TiO_2 and ST-01

Sample	UV	Vis		
	$NO_{x_{\mathrm{removal}}}$ (%)[a]	$NO_{x_{\mathrm{removal}}}$ (%)[a]	NO_x(l_{210})/NO_x(l)[b]	$NO_{x_{\mathrm{removal}}}$ (%)[c]
TiO_2(I)	81.3	68.2	0.59	69.1
TiO_2(N)	81.0	61.7	0.58	57.8
TiO_2(P)	82.3	63.2	0.65	66.5
TiO_2(F)	79.1	0.8	–	–
ST-01	76.6	9.2	–	–

[a] Initial NO_x removal ratio for virgin samples.

[b] Ratio of NO_x concentration after visible light irradiation for 210 min (NO_x(l_{210})) to NO_x(l).

[c] Initial NO_x removal ratio for washed samples.

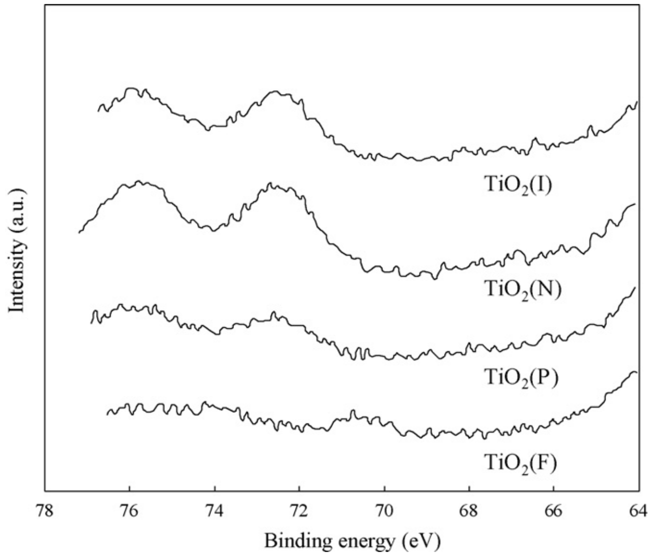

Fig. 5. XPS spectra of Pt-modified TiO_2 samples in the region of the Pt4f band.

TiO_2, no remarkable difference was observed in the region of both Ti2P and O1s among the Pt-modified TiO_2 samples. Fig. 5 shows the XPS spectra of Pt-modified TiO_2 in the region of the Pt4f band. Although every spectrum exhibits broad peaks due to the small amount of Pt, this figure indicates the existence of Pt(II) or Pt(IV) for the samples of TiO_2(I), TiO_2(N) and TiO_2(P). The peak assigned for Pt(0) of which the binding energy is 70.0 eV was observed to be only slight for TiO_2(F). Therefore, it can be concluded that the metallic Pt deposited on TiO_2 in a cluster form does not facilitate the photocatalytic oxidation of NO_x under visible light, as shown in Table 2.

The Cl content and the Cl/Pt atomic ratio in each sample are listed in Table 1. The calculated Cl/Pt atomic ratio of TiO_2(I) was 6.5, which roughly agreed with that of H_2PtCl_6. In aqueous solution, $PtCl_6{}^{2-}$ is hydrolyzed to form an aquo complex or hydroxo complex [24]. The mechanism consists of two hydrolysis steps as follows [25]:

$$[PtCl_6]^{2-} + H_2O \leftrightarrows [PtCl_5(H_2O)]^{1-} + Cl^- \tag{2}$$

and

$$[PtCl_5(H_2O)]^{1-} + H_2O \leftrightarrows [PtCl_4(H_2O)_2]^0 + Cl^- \tag{3}$$

These aquo complexes rapidly dissociate in basic solutions:

$$[PtCl_5(H_2O)]^{1-} + OH^- \leftrightarrows [PtCl_5(OH)]^{2-} + H_2O \tag{4}$$

$$[PtCl_4(H_2O)_2]^0 + 2OH^- \leftrightarrows [PtCl_4(OH)_2]^{2-} + 2H_2O \tag{5}$$

It is clear from these equations that the concentration of $PtCl_6{}^{2-}$ and Cl ions, and pH affect their equilibrium and the fraction of Cl ions among the ligand of each complex. Since H_2PtCl_6 is stable in acidic aqueous solutions, TiO_2(I) prepared by impregnation followed by evaporation of solvent has six Cl ligands, as seen in Table 1. In case of the impregnation method followed by filtration (TiO_2(I′)), the calculated Cl/Pt atomic ratio was 4.2, and this value indicates the presence of the hydrolysis reactions of (2)–(5). In contrast, the Cl/Pt atomic ratio for TiO_2(N) and TiO_2(P) were 2.2 and 0.9, respectively, indicating that the ligand exchange reactions of Cl ions with H_2O were facilitated by the preparation conditions of TiO_2(N) and TiO_2(P). That is, the Cl content decreased in order for TiO_2(I), TiO_2(I′), TiO_2(N) and TiO_2(P). It is concluded from the calculated Pt–Cl coordination number that the approximate ligand composition for TiO_2(N) corresponds to $[PtCl_2(H_2O)_4]^{2+}$ or $[PtCl_2(OH)_4]^{2-}$, and that of TiO_2(P) corresponds to $[PtCl(H_2O)_5]^{3+}$ or $[PtCl(OH)_5]^{2-}$.

Burgeth and Kisch [15] have recently reported that 4-CP in aqueous solution can be photodegradated with Pt(IV)-modified TiO_2 under visible light irradiation. They estimated that chemisorption of $[PtCl_4]^{2-}$ onto TiO_2 forms a covalently bound surface complex having the composition of $\{[Ti]OPtCl_4L\}^{n-}$, $L = H_2O$, OH^-, $n = 1$, 2. We found prior to the present study that any preparation procedure without aging failed to deposit Pt complex onto TiO_2 surface. In contrast, the present Pt modification processes afforded good yields as shown in Table 1. Therefore, we consider from these experimental results that Pt complexes in this study are also chemisorbed to the TiO_2 through Ti–O–Pt bonds.

The similarity in diffuse reflectance spectra and NO_x photooxidation properties among TiO_2(I), TiO_2(N) and TiO_2(P), and the Cl/Pt atomic ratio data strongly suggest that the surface complex formation associated with Ti–O–Pt bonds results in photosensitization, and the Cl ion coordination number in the Pt complex has very little influence.

4. Conclusions

In this study, we have tried to understand the effects of surface-modified platinum chloride on the stimulation of photocatalytic activity in a gas-phase reaction. Pt modification onto TiO_2 surfaces through a wet process greatly increased photocatalytic degradation of NO_x under visible light irradiation. The experimental results demonstrated that Pt-modified TiO_2 with different ligand structures can be synthesized according to the Pt treating procedure. The visible-light-induced photocatalytic activity was correlated with the amount of Pt complex, and not affected by the coordination number of Cl. TiO_2 photocatalysts prepared by quite simple Pt modification processes were proved to work efficiently under visible light irradiation in a gas-phase photocatalytic reaction.

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