Photoactivity of carbon-coated anatase for decomposition of iminoctadine triacetate in water

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Abstract

Carbon-coated TiO_2 were prepared by a simple heat treatment of the powder mixtures of anatase-type TiO_2 (ST-01) with poly(vinyl alcohol) (PVA) at a temperature from 700 to 900 °C. Carbon-coated anatase TiO_2 showed high photoactivity for the decomposition of iminoctadine triacetae (IT) in its dilute solution under UV irradiation. For all carbon-coated TiO_2, the relation between relative concentration of IT in the solution and irradiation time could be approximated to be linear, its slope k corresponding to the rate constant of decomposition reaction of IT molecules. Photoactivity measured by the rate constant k was found to depend strongly on the full width at a half maximum intensity (FWHM) of 1 0 1 diffraction line of anatase phase, i.e., its crystallinity. The highest k value was obtained at around 0.5° in 2θ of FWHM. From repeated uses of the photocatalysts, it was experimentally proved that the pollutants, IT, adsorbed onto carbon layers coated on anatase were able to be decomposed under UV irradiation.
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1. Introduction

Anatase-type TiO_2 have attracted attention of scientists because of its photocatalytic activity for the decomposition of various environmental pollutants, such as NO_x in air and fertilizers in water [1–10]. Various investigations on the preparation of anatase-type TiO_2 were carried out; from titanium tetraethoxide under hydrothermal condition above 250 °C as the particles with 20–30 nm size [11], vapor hydrolysis of titanium tetraisopropoxide at 260 °C as nano-sized particles [12], destabilization of aqueous titanium lactate below 100 °C as thin films on various substrates [13], decomposition of titania-hydrate coated on hollow glass spheres [14], etc. In our previous paper [15], anatase-type TiO_2 powders were synthesized under a simple hydrothermal condition from titanium

oxysulfate $TiOSO_4$ and found to be stable by annealing at 700 °C for 24 h, which resulted in a high crystallinity and high photocatalytic activity, much higher than as-prepared. Photocatalytic activity of anatase was discussed in the relation to the full width of half maximum intensity of X-ray diffraction line [16]. For the photodecomposition of methylene blue in water and diluted NO in air, different crystallinities were found to be required [17].

It was also found that carbon coating of anatase particles was very effective to suppress the phase transformation to rutile, to result in a high crystallinity and consequently to give high photoactivity, even better than the one without carbon coating, in addition to the adsorptivity due to porous carbon layers coated and to prevent the reaction of anatase particles with organic binders [18–20]. On a series of carbon-coated anatase samples, photocatalytic activity was studied for the decomposition of phenol and two azo dyes, methylene blue and reactive black 5, in water [21,22].

On the other hand, outflow of low-concentrated agricultural chemicals for river or sewerage is caused to ill effects in crops and human body. Therefore, resolving of its low-concentrated agricultural chemicals will be expecting in the worldwide. In the present work, photoactivity for the decomposition of iminoctadine triacetate, one of agricultural chemicals, was studied on a series of carbon-coated anatase samples, the same as those used in our previous works [18–22], and was discussed in the relation to the crystallinity of photocatalyst anatase. In order to check the cyclability, the present photocatalysts were repeatedly used.

2. Experimental

Pristine anatase powders were commercially available ones (ST-01, Ishihara-Sangyo Co., Ltd.). Their average particle size measured by X-ray diffraction was about 7 nm, which seemed to make aggregates of about 60 nm under scanning electron microscope. Their BET surface area was rather high as 300 m^2/g.

Carbon coating of these anatase particles was carried out as follows; mixing of poly(vinyl alcohol) in different mass ratios and then heating at a temperature between 700 and 900 °C for 1 h in nitrogen gas flow. Carbon-coated anatase powders were found to keep almost the same morphological features as pristine anatase [18,21]. Without carbon coating, the pristine anatase particles were sintered to grow much larger, consequently BET surface area decreasing to 30 m^2/g after heating to 700 °C and to 2 m^2/g after 900 °C. The details on carbon coating and resulting carbon-coated samples were reported in our previous papers [18,22]. The samples used in the present work are listed in Table 1, with preparation condition, amount of carbon coated and apparent BET surface area.

In order to evaluate the photoactivity of the carbon-coated anatase, iminoctadine triacetate ($C_{24}H_{53}N_7O_6$, guaranteed grade of reagent, IT) was selected. It was used in the rice or orchard field as an insecticide by the contact. IT shows strong bactericidal action to the cause of a disease mycelium. A part of it was often dissolved into field water and came out to water paths in the field, so that it was desired to remove these dissolved IT molecules in order to avoid the contamination of the river.

The sample photocatalyst of 10 mg was dispersed in 1000 mL aqueous solution of IT with the concentration of 100 ppm. The solution thus prepared was irradiated by ultraviolet rays (UV) under stirring. UV irradiation was performed from two black light lamps of 20 W power, intensity of UV rays at the position of the solution being measured to be 11.6 W/m^2. During UV irradiation, 0.7 mL of the solution was sampled and the concentration of IT remained in the solution was determined by a high performance liquid chromatography. Some of photocatalysts were repeatedly used by being transferred to fresh solution of IT with the same concentration of 100 ppm, in order to check the cyclability of carbon-coated anatase.

Adsorption of IT by the sample powders was measured in the dark after the saturation of the concentration change in its solution with initial concentration of 100 ppm.

3. Results and discussion

3.1. Characteristics of carbon-coated anatase

After heat treatment of the mixtures of ST-01 and PVA, the powder thus obtained looked completely black, even the sample SP95-700 and SP90-900 having the smallest amount of carbon coated. From X-ray powder diffraction patterns, the principal crystalline phase was confirmed to be anatase type structure, though the samples heated at 900 °C contained a small amount of reduced phases of TiO_2, such as Ti_4O_7, as summarized in Table 1. X-ray powder patterns of this series of samples were shown in our previous paper [18]. No aggregation of carbon-coated anatase was observed under scanning electron microscope and the anatase particles were reasonably supposed to be covered by thin carbon layer through transmission electron microscopy [18,20].

BET surface area measured on carbon-coated anatase was only apparent value, because of the contributions from two components, anatase and carbon. If the facts that the pristine

Table 1
Samples used in the present work

| Sample code	Preparation condition			Amount of carbon coated (mass%)	BET surface area (m^2/g)	XRD (phases)
	Mixing ratio TiO$_2$/PVA	Temperature (°C)	Residence time (h)			
ST-01	100/0	–	–	0	300	A
SP50-700	50/50	700	1	15	130	A
SP70-700	70/30	700	1	9	120	A
SP90-700	90/10	700	1	5	60	A
SP95-700	95/5	700	1	2	40	A + trace R
SP50-800	50/50	800	1	14	164	A
SP50-900	50/50	900	1	10	170	A
SP70-900	70/30	900	1	8	130	A
SP80-900	80/20	900	1	5	100	A + N
SP90-900	90/10	900	1	2	50	A + N

A: anatase; R: rutile, N: Ti$_4$O$_7$ phase.
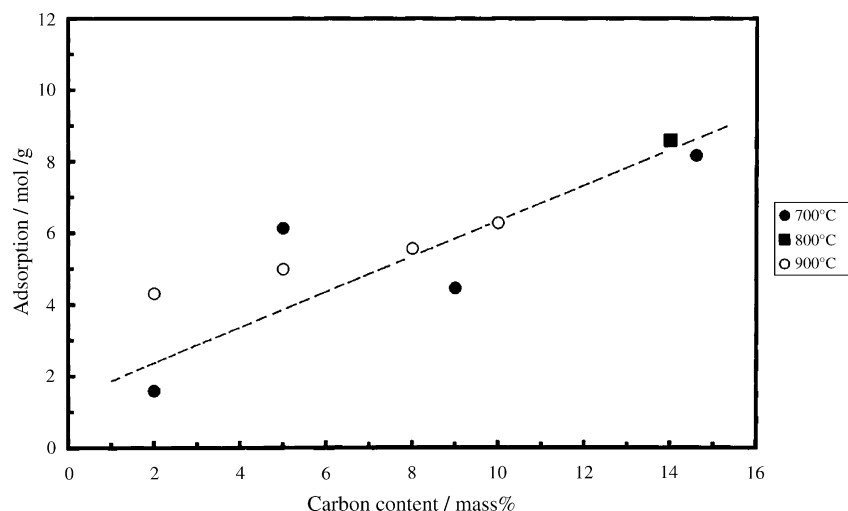
Fig. 1. Relation between adsorption of IT by carbon-coated TiO_2 samples and carbon amount of carbon-coated TiO_2 catalysts obtained from different heat-treatment conditions.

anatase ST-01 gave a small BET surface area, about $30\,m^2/g$ after $700\,°C$ treatment and about $2\,m^2/g$ after $900\,°C$, and also that the main component was anatase, more than 85 mass%, were taken into consideration, however, the carbon layers formed on the anatase particles are reasonably supposed to be responsible for these high apparent BET surface area values observed. The formation of the carbons with high surface area was experimentally proved through the same procedure using MgO as a substrate, which was dissolved out by an acid to isolate the carbon formed [23].

3.2. Adsorption of IT

Adsorption of IT was found to be small on all samples used, in the order of 10^{-5} mol IT/g of carbon-coated anatase. As adsorption of IT into starting TiO_2, ST-01, tried in dark, it became clear that its amount of adsorption was small as well as carbon coating TiO_2. In Fig. 1, the adsorbed amounts of IT into the samples are plotted against amount of coated carbon measured. Even though there is a scattering of the experimental points, adsorption by the present samples depends on the amount of carbon coated.

For the same carbon-coated anatase samples, pronounced adsorption of methylene blue was observed, markedly larger than for pristine anatase ST-01, even though apparent BET surface area measured on carbon-coated anatase was much smaller, $40\text{–}170\,m^2/g$, than that of pristine anatase $(300\,m^2/g)$ [22]. The small adsorption of IT is supposed to be due to a large size of its molecule. Because molecule size of IT was large with ca. 50 nm, it guessed that pores of the suitable size to adsorb it did not exist.

3.3. Photodecomposition of IT

Relative concentration of IT, c/c_0, is plotted in logarithmic scale against irradiation time of UV rays in Fig. 2. The data on

pristine anatase ST-01 are also plotted in the same figure for comparison. Pristine anatase ST-01 gives the fastest decomposition of IT, but for carbon-coated anatase photocatalysts the decomposition proceeds slower than the pristine ST-01, depending strongly on the samples. The sample SP95-700 is close to the pristine ST-01, but the sample SP70-700 and SP90-900 decompose IT more slowly.

For all photocatalysts used in the present work, the relation between $\ln(c/c_0)$ and irradiation time can be approximated to be linear, and so the slope k of the line observed on each photocatalyst was calculated. Here, the slope k corresponds
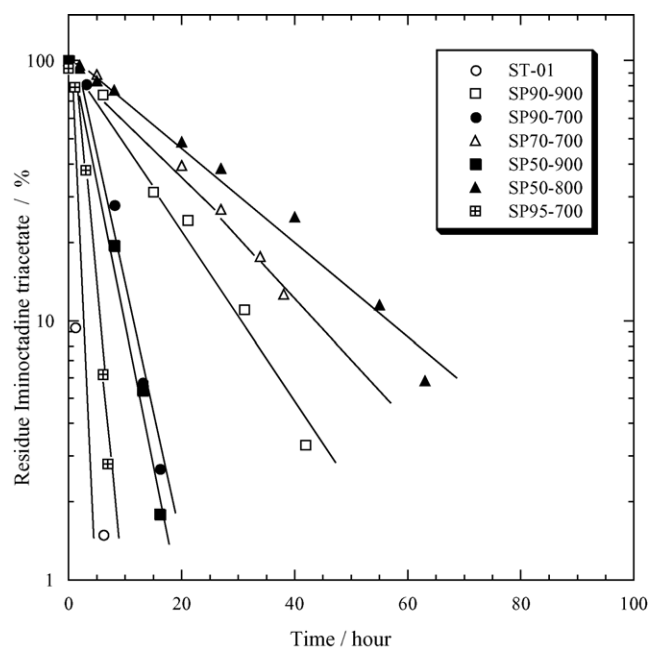

Fig. 2. Changes in relative concentration c/c_0 of IT decomposition under UV irradiation on TiO_2 and carbon-coated TiO_2 catalysts prepared from different contents of PVA and heat-treatment conditions in logarithmic scale.
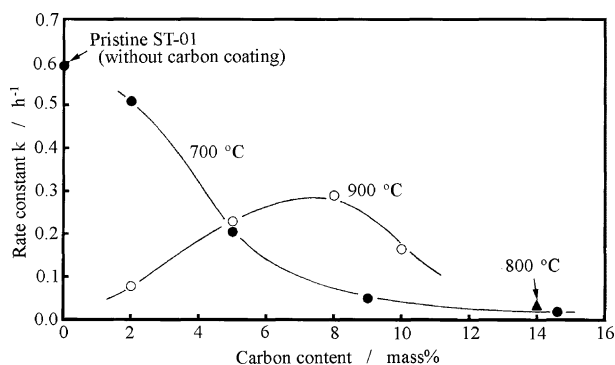
Fig. 3. Relation between rate constant for decomposition of IT by carbon-coated TiO$_2$ samples and carbon amount of its catalysts obtained from different heat-treatment conditions.

Fig. 4. Dependence of rate constant k on FWHM of 1 0 1 diffraction line of anatase of TiO$_2$ without carbon and carbon-coated TiO$_2$ catalysts prepared from different heat-treatment conditions. For convenience, apparent crystallite size is also scaled.

to the rate constant of decomposition reaction of IT molecules which can be approximated by the equation:

$$c = c_0 \exp(-kt)$$

as the case for methylene blue, reactive black 5 and phenol in our previous papers [21,22].

In Fig. 3, rate constant k determined on each photocatalyst is plotted against the amount of coated carbon. For each heat treatment temperature, 700 and 900 °C, k depends on the amount of carbon coated, but its dependence is completely different from each other; by 700 °C treatment k decreases with increasing carbon content, but k shows a maximum at around 8 mass% of carbon at 900 °C. Although thickness of carbon layer coated on anatase particles could not be determined directly, it is reasonably supposed that the higher is the amount of coated carbon the thicker is the carbon layer on anatase. Therefore, the result shown in Fig. 3 suggests that the decomposition rate observed on the carbon-coated anatase depends on different parameters, thickness and porosity of carbon layers coated.

For anatase powders synthesized either under hydrothermal condition or sol–gel method, rate constant k measured on photodecomposition of methylene blue was reported to depend on full width at half maximum intensity (FWHM) of 1 0 1 diffraction line of anatase phase and showed that a narrow range of FWHM gives high rate constant [16,17]. For the present series of carbon-coated anatase, the rate constants for the decomposition of some dyes, methylene blue and reactive black 5, and phenol were discussed as a function of FWHM of anatase phase [21,22]. Rate constant k for the decomposition of IT in the present work is also plotted against FWHM of 1 0 1 diffraction line, as shown in Fig. 4.

Though the number of samples was limited and there was scattering of the experimental points, the highest k is given at the FWHM of around 0.5° (Cu Kα) although it is a little smaller than the k-value for the pristine ST-01. For the decomposition of other molecules, using the same carbon-coated anatase, very similar dependences of k on FWHM of anatase phase were observed [21,22]. In the case of methylene blue,
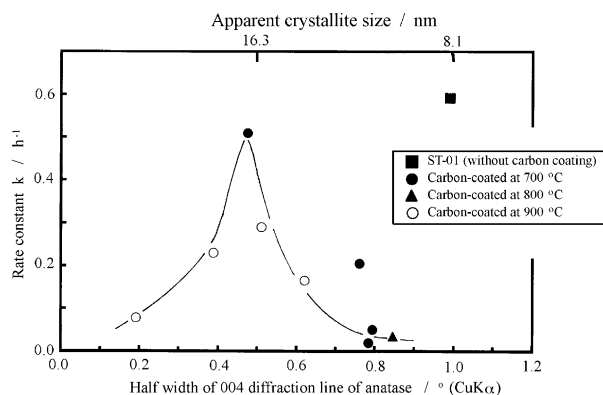
of which a large amount was adsorbed into the carbon layers coated, the largest k value was much higher than the pristine ST-01. In other molecules, including the present IT, even the largest k value observed on the present carbon-coated anatase could not overcome the k value of the pristine ST-01 (without carbon coating) and their adsorption into carbon-coated photocatalysts was not so large.

Often crystallite size calculated from the observed FWHM using Sherrer's equation. However, it is known that the FWHM is due to both crystallite size and lattice strain, so that the reported values of crystallite size is only apparent values, neglecting the contribution of lattice strain. The present pristine anatase ST-01 consisted of small primary particles of about 7 nm size and gave very broad diffraction lines of X-rays, which may suggest the presence of a large amount of lattice strain. Even after heat treatment at 900 °C, the diffraction lines for carbon-coated anatase were broad [18], revealing no marked annealing in structure. Therefore, the contribution of lattice strain to the broadening of diffraction lines might not be negligibly small in most of the present samples. This is the reason why FWHM was used to characterize the crystallinity of the samples in Fig. 4. For comparison, however, the scale of apparent crystallite size, neglecting lattice strain, was shown in Fig. 4.

3.4. Cyclic performance of carbon-coated anatase

In order to check cyclic performance, the present photocatalysts were repeatedly used. In Fig. 5, the plots of $\ln(c/c_0)$ versus irradiation time for first and second cycles of photodecomposition of IT by using the same photocatalysts are shown. The samples of photocatalyst were kept first in the dark for 200 h to saturate the adsorption of IT and then exposed to UV irradiation (first cycle). After about 100 h, the sample was separated from the test solution by filtering and then dispersed again into a virgin solution with 100 ppm concentration, being again kept in the dark for about 200 h and then irradiated by UV (second cycle).
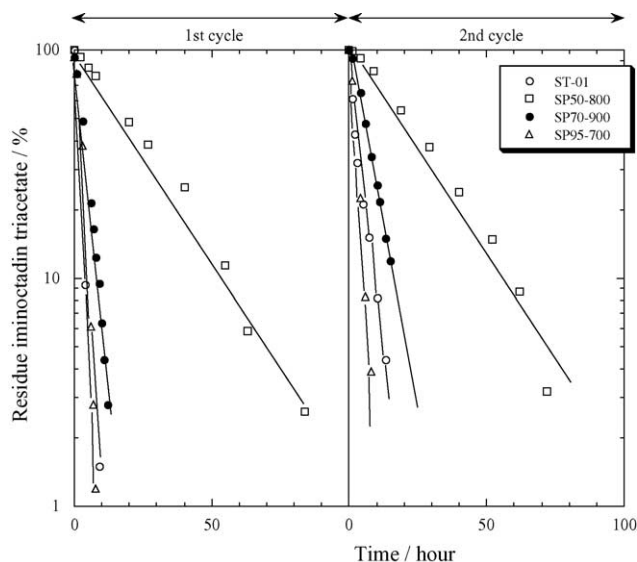
Fig. 5. Cycling performance of IT decomposition with changes in relative concentration c/c_0 under UV irradiation in logarithmic scale.

In the dark, relative concentration change before second cycle irradiation was very little, revealing that the carbon layer was almost saturated by IT. By UV irradiation, however, abrupt decreases in IT concentration are observed in the second cycle, as fast as in the first cycle. Therefore, IT molecules in the solution were decomposed by the photoactivity of carbon-coated anatase. No marked difference in the rate constant k of decomposition reaction of IT molecules, i.e., the slope of the lines in Fig. 5, on first and second cycle was recognized. From these results, cyclic performance for decomposition of IT and reusing of carbon-coated anatase were revealed. By taking into consideration of the fact that the pollutant IT molecules have to be adsorbed into carbon layer coated and then diffuse to anatase surface through carbon layer, the present results on cyclic use of carbon-coated anatase reveals that adsorbed IT is decomposed by the substrate anatase.

4. Conclusion

For carbon-coated anatase, photocatalytic activity for the decomposition of iminoctadine triacetate was experimentally approved, which showed the same dependence on FWHM of 1 0 1 diffraction line of anatase phase. Hybridization of photoactivity with adsorptivity is expected to open new applications of both photocatalyst anatase-type TiO_2 and adsorptive porous carbons. It was experimentally proved that the pollutants adsorbed onto carbon layers were able to be decomposed under UV irradiation. The present results seem to propose a possibility of application of these hybrid materials for water purification. For practical application, the control of rates of adsorption and photodecomposition is desired to get appropriate combination of these two functions. The possibility of cyclic use of the present carbon-coated anatase is also promising for practical applications.

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