JOURNAL OF Materials CHEMISTRY

Carbon coating of anatase-type TiO_2 and photoactivity

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Received 22nd February 2002, Accepted 4th March 2002

Carbon coating of photocatalytic anatase-type TiO_2 powders was successfully carried out by heating a powder mixture of poly(vinyl alcohol) and TiO_2 under N_2 gas flow at temperatures above 700 °C. All particles of TiO_2 were covered by a carbon layer and looked black. For methylene blue (MB) in aqueous solution, carbon-coated anatase powders thus prepared showed marked adsorption and decomposition under UV irradiation and were confirmed to keep almost the same photoactivity as that without any carbon coating. Carbon coating of anatase-type TiO_2 was found to give different merits for photoactive performance; suppression of phase transformation from anatase to rutile at high temperatures, quick adsorption of MB into the carbon layer, decomposition of adsorbed MB by TiO_2 and prevention of the interaction of TiO_2 with binder resin. Repeated cycles of adsorption and decomposition of methylene blue in aqueous solution were experimentally confirmed.

1. Introduction

Environmental pollution by NO_x in air and various organic compounds in water has caused various serious problems for human health. The decomposition of these pollutants using TiO_2 photocatalysts has been one of the most promising methods for dealing with the problem,[1–9] and now these photocatalysts have started to be utilized as filters, built into purification systems for air and water, and also as paints and coatings for walls, building blocks, tiles, window glasses, tents, *etc.*[10–14]

For some practical applications, the particles of photocatalyst TiO_2 were either mounted on adsorbents, such as activated carbons and zeolites, or fixed on a substrate by using a binder. In the former case, the pollutant molecules could be adsorbed onto adsorbents, but they were not readily decomposed by the TiO_2 photocatalyst mainly because of the slow diffusion speed of the pollutants on the adsorbent surface to the TiO_2 particles. Consequently, the adsorbent was saturated with pollutants during long-term use and so only photocatalytic decomposition of the pollutants by the TiO_2 particles themselves was observed. In the latter case, organic polymer binders were not suitable, because the binder was decomposed by the photocatalytic reaction on the TiO_2 particles, as well as the pollutants. Therefore either ceramics or fluorinated resins had to be used as binders, which led to increased costs.

In the present work, TiO_2 particles were coated with a carbon layer in order to give adsorption ability to the catalyst particles, to transfer the adsorbates to the surface of the TiO_2 and also to prevent direct contact of the TiO_2 with the binder polymer. The carbon-coated anatase-type TiO_2, in practice, could keep almost the same photocatalytic activity as that without the carbon coating, in addition to the adsorption ability of the carbon layers, and could prevent the decomposition of the polymer binder.

2. Experimental

2.1 Sample preparation

Carbon coating of the TiO_2 powders was achieved by following the same procedure as that reported in a previous paper;[15] powder mixtures of TiO_2 with a carbon precursor polymer in different ratios were heated in a flow of nitrogen at different temperatures of 700 to 1100 °C for 1 h. In the present work, a commercially available TiO_2 powder with an anatase-type structure (ST-01, Ishihara-Sangyo Co. Ltd) was selected as the starting material, of which the average size of primary particles was determined to be 7 nm by means of X-ray diffraction (XRD), and that of aggregated secondary particles was about 60 nm by SEM. As a carbon precursor polymer, poly(vinyl alcohol) (PVA, Nippon Synthetic Chem. Ind. Co. Ltd) with an average degree of polymerization of 2000 and particle size under 850 μm was used. The TiO_2–PVA mixtures with 5, 10, 30 and 50 mass% PVA were prepared. The heating rate to the programmed temperature was 10 °C min^{-1} and flow rate of nitrogen was 100 mL min^{-1}. After heat treatment the powders were cooled down to room temperature in a flow of nitrogen. The preparation conditions, mixing ratio of PVA and heating temperature and time, are listed in Table 1, together with the sample code used in the present paper.

For each sample the X-ray diffraction (XRD) pattern was measured with Ni-filtered CuKα radiation and a scanning speed of 2° min^{-1}, and carbon content was determined from the weight loss of the sample heated at 500 °C for 1 h in air. For some samples, the BET surface area was measured by nitrogen adsorption at 77 K.

2.2 Adsorption and photocatalytic decomposition of methylene blue

Methylene blue (MB, $C_{16}H_{18}N_3S$, reagent grade) was dissolved in purified water to a concentration of 2.94×10^{-5} and

DOI: 10.1039/b201942f

Table 1 The samples prepared in the present work

Sample code	Catalyst/carbon precursor	Heating temperature and time	Mixing ratio of PVA (mass%)	Carbon content (mass%)	BET surface area/m^2 g^{-1}
ST-01	—	—	0	0	300
ST-01-700	—	700 °C, 1 h	0	0	30
SP50-700	ST-01/PVA	700 °C, 1 h	50	16	130
SP70-700	ST-01/PVA	700 °C, 1 h	30	9	120
SP90-700	ST-01/PVA	700 °C, 1 h	10	5	60
SP95-700	ST-01/PVA	700 °C, 1 h	5	2	40
SP50-800	ST-01/PVA	800 °C, 1 h	50	14	
SP50-900	ST-01/PVA	900 °C, 1 h	50	10	170
SP50-1000	ST-01/PVA	1000 °C, 1 h	50	12	
SP50-1100	ST-01/PVA	1100 °C, 1 h	50	9	

1.47×10^{-4} mol L^{-1}. Powder samples of 0.021 g were dispersed into 40 mL of 2.94×10^{-5} mol L^{-1} MB solution thus prepared in a glass bottle with a screw cap. The bottle was stirred either in the dark or under UV rays of about 1 mW cm^{-2} from a black light (10 W) in a box. The blue color of the solution faded gradually with time due to the adsorption and decomposition of MB. The speed of color fading was followed by sampling 3 mL aliquots of the solution at appropriate intervals and measuring the optical absorbance at a wavelength of 650 nm, which was attributed to MB. From the experiments in the dark, the adsorption of MB into the samples could be followed. In the experiments under UV irradiation, the color fading was due to both adsorption and decomposition of MB by the sample powders. In the present work, therefore, sample powders saturated with MB were prepared and transferred into 40 mL of MB solution with 2.94×10^{-5} mol L^{-1} with stirring under UV irradiation. The saturated samples were prepared by dispersing in a ten-times concentrated MB solution (2.94×10^{-4} mol L^{-1}) with stirring in the dark. After no change in optical absorbance of the solution was detected, though MB still remained in the solution, the samples were isolated by centrifuging, and then washed with water. There was little extraction of MB from the samples thus treated during washing with water and so these samples were considered to be saturated or nearly saturated by MB. The decomposition of MB using these saturated samples was followed by measuring the optical absorbance of the solution as a function of UV irradiation time. The value of pH of the MB solution was kept around 6–7 during the photocatalytic reaction with different samples.

In order to measure the cyclic performance of adsorption and photocatalytic decomposition of MB, sample powders prepared from the mixture with 50 mass% PVA at 900 °C (SP50-900) were mounted on a slide glass using a styrene–butadiene base latex binder; the slurry of SP50-900 powders with a latex emulsion (Nipol LX430, Nippon Zeon Co., Ltd) in a mass ratio of 80 : 20 was spread on a slide glass and then dried at 150 °C for 10 min. Two slide glasses holding 0.034 and 0.015 g of SP50-900 were prepared. The former was immersed in 40 mL of 2.94×10^{-5} mol L^{-1} MB solution and the latter in 40 mL of 1.47×10^{-4} mol L^{-1} MB solution with stirring under UV irradiation. When the optical absorbance at 650 nm of the solution became almost zero, the slide glass was taken out from the solution and again immersed in new MB solution with the same concentration under UV irradiation with checking the change in optical absorbance with time.

2.3 Interaction with acrylic resin

The interaction between photocatalytic TiO_2 particles and binder was studied by using a combination of the sample powders prepared from the mixture with 50 mass% PVA at 700 °C (SP50-700) and an acrylic resin (A-166, Dainihon-Ink Chem. Ind. Co. Ltd). The acrylic resin was diluted with propan-2-ol to a concentration of 20 mass%. Into the solution the sample powders SP50-700 were mixed in a mass ratio of acrylic resin to carbon-coated TiO_2 of 80 : 20 by using a mixer with 15 000 rpm for 15 min. The mixed solution was spread on a slide glass and dried at 120 °C for 5 min. The film thus obtained was exposed to UV rays with about 1 mW cm^{-2} from a black light (10 W) in a box. Weight loss with UV irradiation time was measured at appropriate intervals. Two acrylic resin films containing no photocatalysts and those without carbon coating (*i.e.*, ST-01) were also examined.

3. Results and discussion

3.1 Structure and morphology of carbon-coated TiO_2

The samples obtained after heating with PVA above 700 °C looked black, though the original ST-01 remained white after heating. Therefore, the particles of TiO_2 were covered with carbon which was produced by the carbonization of PVA. The carbon coating of solid particles has been reported on various ceramics, including graphite, and metals.[15–20] SEM micrographs of samples, ST-01, ST-01-700, SP95-700 and SP50-700, are shown in Fig. 1. In the original ST-01, aggregated secondary particles with a size of around 60 nm are observed (Fig. 1a), though the size of primary particles is supposed to be one tenth that of secondary particles. After 700 °C heating, *i.e.*, in ST-01-700, most of the particles are sintered with each other, becoming larger than 1000 nm, though a small amount of small particles still remain (Fig. 1b). For SP95-700 and SP50-700, however, the particle size observed under SEM is kept almost the same as the original ST-01, around 60 nm, even though they have been heated at 700 °C, as shown in Fig. 1c and 1d, respectively.

In Table 1, the carbon content (the carbon residue after the carbonization of PVA) in each sample is listed. It decreases with decreasing mixing ratio of PVA and therefore, it may be controlled by changing the PVA mixing ratio. The carbon content in the sample also decreases with increasing heating temperature; 16 mass% after heating at 700 °C and 9 mass% at 1100 °C for a PVA mixing ratio of 50 mass%.

The values of BET surface area of some samples are shown in Table 1. The original ST-01 has a rather high surface area of about 300 m^2 g^{-1}, but after heating up to 700 °C the surface area becomes one tenth of the original value, 30 m^2 g^{-1}, because of sintering of the particles. The surface area of carbon-coated TiO_2 samples also decreased to below 130 m^2 g^{-1} after heating at 700 °C, because of slight sintering and crystal growth of the TiO_2 particles. If the surface area of TiO_2 particles coated by carbon after 700 °C heating is the same as those heated without the carbon layer (ST-01-700), the surface area for carbon layers is rather high, about 500–600 m^2 g^{-1}. However, it was not possible to measure the surface area for carbon and TiO_2 separately.

In Fig. 2a, XRD patterns of the samples heated with 50 mass% PVA at different temperatures (the samples SP50-700 to SP50-1100) are shown. The anatase-type structure is kept even after heating at 1100 °C, though small amounts of

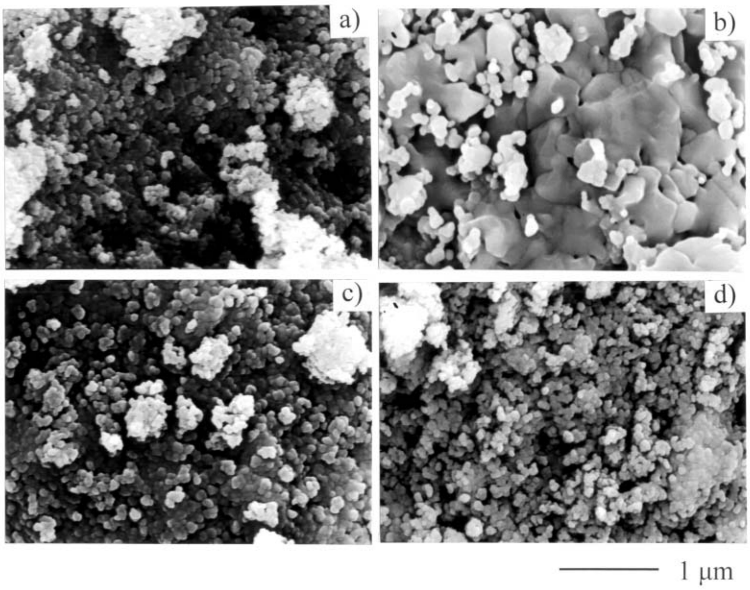

Fig. 1 SEM micrographs of the samples ST-01 (a), ST01-700 (b), SP95-700 (c) and SP50-700 (d).

the unknown phase marked by filled circles in the figure and also a rutile-type structure marked by open circles appear above 900 °C. As shown in Fig. 2b, on the other hand, the original ST-01 without carbon coating has an anatase-type structure, but it is partly transformed to a rutile-type structure even at 700 °C.

In the present work, the identification of the unknown phase appearing in Fig. 2a could not be performed mainly because of its formation in only small amounts. However, it was proved to be a Ti_4O_7 phase, which is reasonably supposed to be formed by the reduction of TiO_2 by coated carbon, by using fine particles synthesized through the hydrolysis of titanium alkoxides and has almost the same photocatalytic activity as anatase.[21]

The crystallinity of the sample ST-01 is improved by heating to 700 °C, as indicated by sharpening of all the diffraction lines, typically by a separation of 103, 004 and 112 diffraction peaks at around 38° in 2θ. The improvement in crystallinity is not so pronounced in the carbon-coated samples SP50-700 and SP50-800; broad diffraction lines are seen, with no separation among the three diffraction peaks mentioned above. This XRD measurement agreed with the SEM observation and surface area measurement, which showed sintering of the TiO_2 particles on heating. Above 900 °C, the diffraction lines for the anatase-type structure are sharpened and the separation of these three diffraction peaks becomes clear, but at the same time a rutile phase appears (Fig. 2a).

The PVA mixing ratio has an influence on structural change in anatase, as shown in Fig. 2c. With decreasing PVA mixing ratio, *i.e.*, with consequent decreasing carbon content in the resultant samples, the crystallinity of the anatase-type structure is improved. In the samples with 10 and 5 mass% PVA (SP90-700 and SP95-700), a rutile-type structure is formed, but

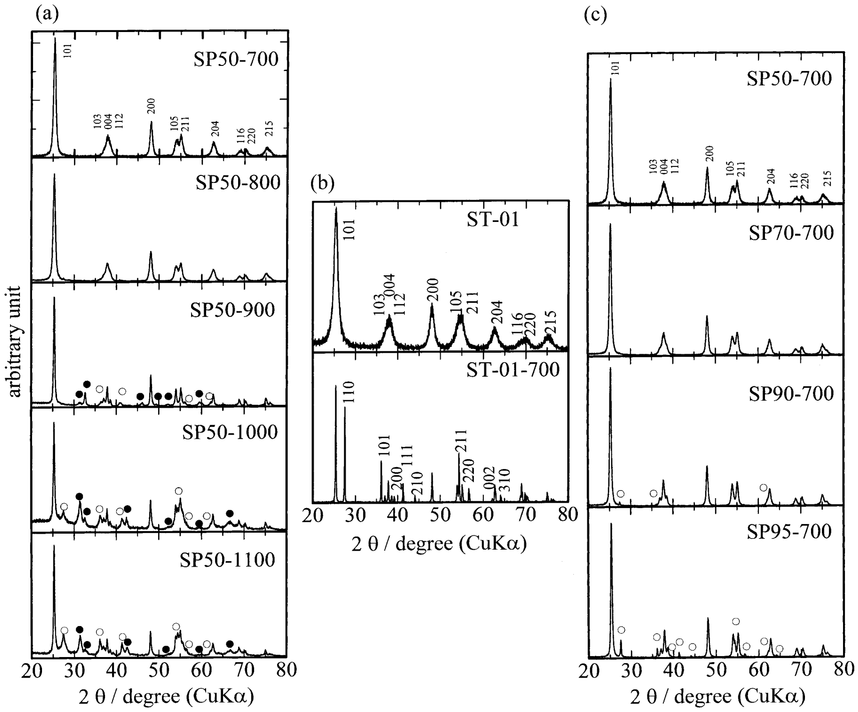

Fig. 2 XRD patterns of the samples heated to different temperatures. a) The samples heated at different temperatures, ●: unknown phase, ○: rutile phase, b) the original ST-01 and ST-01-700 (ST-01 heated at 700 °C), c) the samples produced from different mixing ratios of TiO_2 and PVA.

other samples with 30 and 50 mass% PVA are a single anatase phase.

In the XRD patterns for all carbon-coated samples (Fig. 2a and c), the diffraction peaks of carbon were not observed because of the low carbon content and also low crystallinity as so-called amorphous carbon.

For ST-01, the particles observed under SEM are supposed to be aggregates of small crystals whose size may be comparable with the average crystallite size of 7 nm determined by XRD. The particles of the original sample ST-01 were sintered during heating and became much larger, as seen in ST-01-700 (Fig. 1b). During heating the growth of crystals occurred at the same time, which was shown by the sharpening of the diffraction lines (Fig. 2). In the carbon-coated samples, however, not only sintering of the aggregated particles but also crystal growth in each particle were depressed, the apparent size of carbon-coated samples being not so much different from the original ST-01 and all diffraction lines being broadened as the original showed. The reduction in sintering and crystal growth may be responsible for the suppression of the phase transformation from anatase to rutile at high temperatures. The same effect of suppression of the transformation to rutile was observed on the anatase powders which were coated by carbon from a different precursor.[22] However, the detailed mechanism for the suppression of phase transformation from anatase to rutile by carbon coating requires more experimental results to be understood.

3.2 Adsorption and photocatalytic activities of carbon-coated anatase

In Fig. 3a, color fading of the MB solution in the dark, which is due to the adsorption of MB into the sample particles, was shown on the samples with different carbon contents heated at 700 °C (ST-01-700 and SP50-700 to SP95-700), together with the original ST-01. The original ST-01 and ST-01-700 adsorb MB very slowly, and about 39% of MB is absorbed after 15 h. Complete color fading of MB of the solution with these samples took more than 120 h. However, carbon-coated samples show marked adsorption of MB. Samples SP50-700 and SP70-700, which have high carbon contents, adsorb all the MB in the solution within 10 min. The color fading curves for samples SP90-700 and SP95-700 with low carbon contents seems to occur in two steps, very quick fading in the beginning and then a slow one; in the first step color fades down to about 3 and 26%, respectively, and then the complete adsorption of the rest of the MB in the solution takes about 15 and 25 h, respectively.

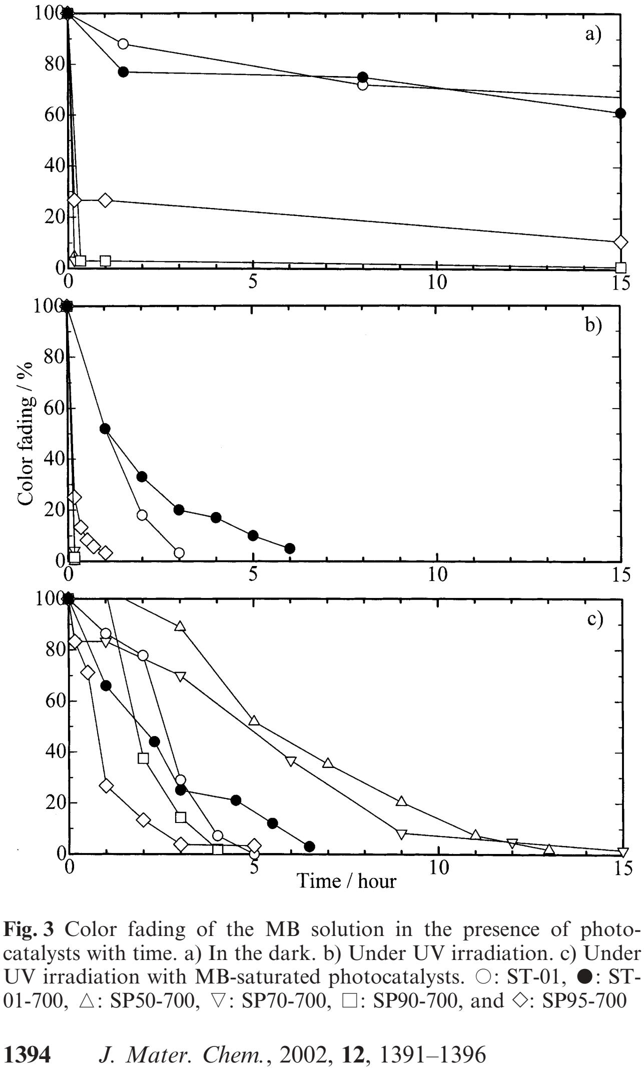

Fig. 3 Color fading of the MB solution in the presence of photocatalysts with time. a) In the dark. b) Under UV irradiation. c) Under UV irradiation with MB-saturated photocatalysts. ○: ST-01, ●: ST-01-700, △: SP50-700, ▽: SP70-700, □: SP90-700, and ◇: SP95-700

These results clearly show two types of adsorption of MB into carbon-coated TiO_2 particles; rapid and slow adsorption. The former is the adsorption of MB into the micropores of the coated carbon layer which is supposed to have a high surface area (Table 1), similar to that of activated carbons. The latter is observed on the particles of ST-01 and ST-01-700; ST-01 and ST-01-700 adsorbed slowly onto their aggregated particles, which looked blue at the end of adsorption. From the present results in Fig. 3a, the speed of color fading can be concluded to be much faster for the former than for the latter.

It was experimentally shown that the high crystallinity of the anatase phase on photocatalytic decomposition of MB and ipconazole (a kind of fungicide) is an important factor for a high decomposition speed,[23–25] even though the surface area decreases markedly. Partial transformation to rutile was shown to reduce the photocatalytic activity of TiO_2 catalysts through the determination of the optical band gap.[25] The improvement in the crystallinity of anatase was reported to be advantageous for MB decomposition, and the decrease in specific surface area due to the grain growth and also phase transformation to rutile by heating were also reported to be unfavorable for MB decomposition.[23] In the sample ST-01-700, these three factors, improvement in crystallinity, decrease in surface area and phase transformation to rutile, occurred at the same time. This might be the reason why ST-01 and ST-01-700 showed similar behavior for MB decomposition, as shown in Fig. 3a.

Color fading of the MB solution under UV irradiation in the presence of the present samples is shown in Fig. 3b. Color fading curves for SP50-700 and SP70-700 are not differentiated from those in the dark, indicating that apparent color fading is governed by the adsorption of MB into these particles. On SP95-700, however, fading is accelerated by UV irradiation; in the dark MB color fades to about 26% after 10 min and then to 2% after 25 h (Fig. 3a), but under UV irradiation it becomes zero after only 1 hour. A similar but a little less accelerated effect is observed for SP90-700. For ST-01 and ST-01-700, on the other hand, color fading is much faster than that without UV irradiation, but it is still slower than that observed on carbon-coated samples. It has to be mentioned that the particles of ST-01 and ST-01-700 are never colored during UV irradiation.

These results indicate that photocatalytic decomposition of MB certainly occurs on TiO_2 particles, even on those coated by carbon, and that MB adsorption and decomposition were performed on carbon-coated particles, the former looking faster than the latter.

In Fig 3c, the fading behavior of the MB-saturated samples under UV irradiation are shown. For the original ST-01, fading speed is rather slow in the beginning, probably because the decomposition of adsorbed MB is the main photocatalytic reaction, and then fading occurs rapidly due to the decomposition of MB in the solution, but it needs about 5 h for the complete decomposition. For MB-saturated ST-01-700, fading speed is also slower in comparison with that for non MB-saturated ST-01-700. The results for ST-01 and ST-01-700 reveal that adsorbed MB is reasonably supposed to be decomposed before MB in the solution. On carbon-coated samples, the same sequence of photocatalytic decomposition of MB could be assumed; SP95-700 and SP90-700 which have small carbon contents and small adsorption capacities show rapid fading of the MB solution, faster than the original ST-01, but SP70-700 and SP50-700 fade the color much more slowly than ST-01. The low apparent photoactivity for SP70-700 and SP50-700 with high carbon contents seems to be caused by two factors. First, in SP50-700 and SP70-700, a relatively large amount of MB is adsorbed into the carbon layers very quickly, but it is supposed to take time for the adsorbed MB in the carbon layers to diffuse to the surface of the TiO_2 particles. Secondly, UV irradiation is supposed to become weaker during passing through the coated carbon layer.

In Fig. 4, color-fading behaviors of the carbon-coated samples with different heating temperature are compared with the original ST-01. With increasing heating temperature up to 900 °C, the fading speed becomes faster, probably because of the improvement of crystallinity of the anatase-type structure, and above 900 °C the color fading speed decreases, which is supposed to be mainly because of the partial transformation of anatase to rutile in the TiO_2 aggregates. For SP50-1000 and SP50-1100, with increasing rutile (Fig. 2a), the color fading speed tends to be reduced.

In the present work, color fading was principally followed by a decrease in absorbance at 650 nm wavelength. It is worth mentioning that the same absorbance decrease was observed at wavelengths around 250–300 nm.

The present experimental results clearly show that color fading of the MB solution is due to the adsorption and decomposition of MB, and the MB adsorbed in the carbon layer is decomposed by UV irradiation of the TiO_2 particles. The suppression of the phase transformation from anatase to rutile by carbon gives certain advantages for the present carbon-coated catalysts.

3.3 Cycle of adsorption and photocatalytic decomposition of MB

To confirm that a cycle of adsorption and photocatalytic decomposition is possible on the present carbon-coated anatase-type TiO_2, the sample SP50-900 was selected, because it has the highest speed of apparent photocatalytic decomposition among the present samples. The color fading with cycling is shown in Figs. 5a and b.

The result in Fig. 5a, where the concentration of MB is 2.94 × 10^{-5} mol L^{-1}, proves clearly that cyclic usage of carbon-coated anatase-type TiO_2 is possible and no detectable reduction in photocatalytic activity is observed. Even in higher concentration MB solution (1.47 × 10^{-4} mol L^{-1}) in Fig. 5b, the same cycling performance is confirmed. The fading rate appears to decrease with cycling in Fig. 5a, which seems to be due to adsorbed MB and its decomposition products remaining in the carbon layers and also at the side in contact with the slide glass, where the UV rays could not reach. This is reasonably supposed to be related to the experimental procedure in Fig. 5a, transferring the catalysts before reaching complete fading. In Fig. 5b, therefore, UV irradiation was continued even after complete fading. A long irradiation time even after the solution faded to zero absorbance (period shown by arrows in Fig. 5b) seems to give faster fading speeds at the beginning of the following cycle, suggesting that the complete decomposition of MB adsorbed into the carbon layers is performed during this irradiation period.

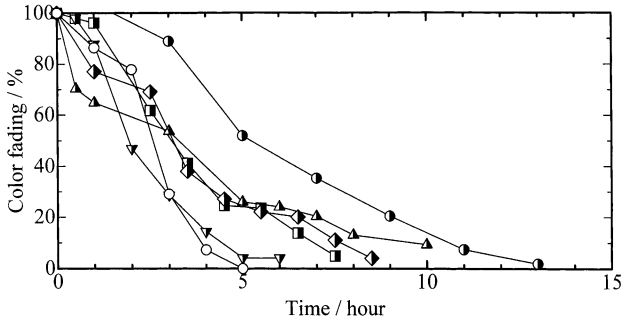

Fig. 4 Color fading of the MB solution under UV irradiation in the presence of MB-saturated photocatalysts heated to different temperatures. ◑: SP50-700, ◭: SP50-800, ⧩: SP50-900, ◨: SP50-1000, and ⬗: SP50-1100, ○: ST-01

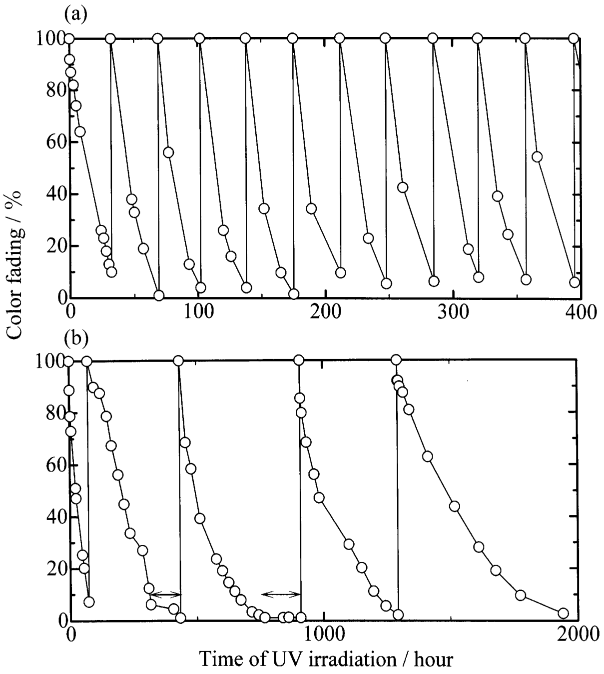

Fig. 5 Color fading of the MB solution under UV irradiation in the presence of the sample SP50-900 with cycling to use fresh MB solution. Arrows represent the transfer of the SP50-900 sample into fresh MB solution. a) 2.94 × 10^{-5} mol L^{-1} MB solution, b) 1.47 × 10^{-4} mol L^{-1} MB solution.

3.4 Interaction with acrylic resin

In Fig. 6, weight loss under UV irradiation with time is compared among three acrylic resin films, the film without any photocatalysts, that containing the original ST-01 and that containing carbon-coated sample SP50-700. The film containing ST-01 decreases its weight quite rapidly and reaches 39% loss after 870 h, which is mainly due to the photocatalytic decomposition of the resin by TiO_2, as pointed out by many authors. However, the film containing SP50-700 shows only 5% loss even after 870 h irradiation, which is almost the same as the acrylic resin film without any photocatalyst, which is

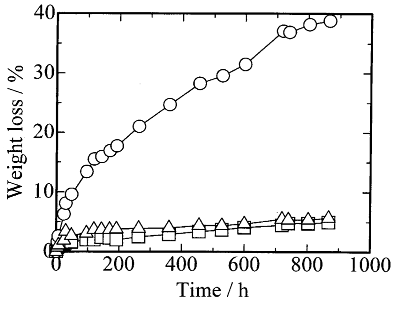

Fig. 6 Weight loss of photocatalysts dispersed in acrylic resin under UV irradiation. ○: acrylic resin with ST-01 △: acrylic resin with SP50-700, □: acrylic resin without photocatalysts.

reasonably supposed to be due to the evaporation of the organic solvent remaining from film casting.

The present result reveals that carbon coating on TiO_2 particles works effectively to prevent the interaction with binder resins.

4. Conclusion

Photocatalyst anatase-type TiO_2 particles were coated with a carbon layer by mixing TiO_2 particles with PVA and then heating above 700 °C under N_2 gas flow. The presence of carbon layers on coated TiO_2 particles was found to give various advantages to the photocatalytic TiO_2 particles; suppression of the phase transformation of anatase to rutile structure by preventing the sintering and crystal growth in TiO_2 particles, quick adsorption of MB to transfer it to the surface of TiO_2 where it undergoes decomposition under UV irradiation, and also prevention of the interaction between TiO_2 and binder polymer which decomposes the polymer under UV irradiation. The cycle of adsorption and photocatalytic decomposition of MB was confirmed. The performance of the photocatalyst observed on carbon-coated samples, particularly heated up to 900 °C, is promising for practical applications.

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