Preparation and characterization of carbon-coated TiO₂ photocatalysts – Hybridization of photocatalytic activity and adsorptivity for purification of water –

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Carbon-coated TiO₂ were prepared by a simple heat treatment of the powder mixtures of anatase-type TiO₂ (ST-01) with carbon precursor, poly (vinyl alcohol) (PVA), hydroxyl propyl cellrose (HPC) and poly (ethylene telephthalate) (PET) etc., at a temperature of 700 to 900 °C. Diffuse optical reflectance spectra for carbon-coated TiO₂ clearly showed the absorption edge for anatase-type structure, overlapping with absorption due to coated carbon over all wavelength of 220-850 nm. Photocatalytic activity of carbon-coated TiO₂ was evaluated through the determination of rate constant *k* for the decomposition of four model pollutants in water, methylene blue (MB), reactive black 5 (RB-5), phenol (Ph) and iminocadine triacetate (IT), under UV irradiation. For MB most of carbon-coated TiO₂ showed higher activity than the pristine anatase powder, but for others carbon-coated anatase gave either comparable or smaller rate constant for their photodecomposition. Photocatalytic activity defined by rate constant *k* for pollutants decomposition was found to depend strongly on crystallinity of anatase phase, which was evaluated by full width at half maximum intensity (FWHM) of 101 diffraction line; a maximum of *k* at an apparent FWHM of about 0.6° in 2θ (CuKα) for four pollutants. Adsorptivity of carbon-coated TiO₂ photocatalysts was determined and discussed on the relations to BET surface area, amount of carbon coated and also rate constant *k* for the decomposition of MB, RB5, Ph and IT. Adsorptivity of carbon-coated catalysts depends strongly on the adsorbate (pollutant) but also on the surface nature of carbon layer on TiO₂ particles. The relations between adsorptivity and rate constant *k* for four pollutants looked similar, suggesting that the pollutant adsorbed in the larger amount being decomposed with the higher rate. In order to check cyclic performance of carbon-coated TiO₂, the photocatalysts were repeatedly used either in powder or fixed on one side of double-sided organic adhesive tape. It was proven that the carbon-coated TiO₂ could be resisted to the multiple usage without marked deterioration in rate constant. The merits and demerits of carbon coating on photocatalyst TiO₂ particles were discussed.

KEYWORDS : Anatase-type TiO₂, Photocatalysis, Carbon coating, Adsorptivity, Methylene blue

1. Introduction

Recently, titanium dioxide TiO₂ with anatase structure was found to reveal photocatalytic activity under ultraviolet (UV) irradiation, and used for the improvement of our environment through the purification of air and water. Various fundamental and technological researches have been carried out and a part of the results in those researches are already using in our life, such as ceramic tile to decompose the organic pollutants and self-cleaning glasses for windows^{1), 2)}. We found that some advantages were obtained by carbon coating on TiO₂ crystalline particles having anatase structure as photocatalysts^{3), 4)}. Carbon coating suppressed

the phase transformation from anatase to rutile phase and anatase phase could have high crystallinity which is advantageous in order to get high photocatalytic activity for water purification, in addition to have adsorptivity due to porous carbon layers coated and to prevent the reaction of anatase particles with organic binders⁴⁾⁻⁸⁾. It was experimentally shown that the suppression of phase transformation was due to the hindrance of sintering between anatase particles by carbon layers⁶⁾, and was efficient with carbon coating over 5 mass %⁸⁾. Carbon layer coated on TiO₂ particles was supposed to be porous⁹⁾ and responsible for a large adsorption ability for pollutants in water, such as methylene blue (MB)^{7), 8)}.

Coupling of a large adsorptivity with a high photocatalytic activity

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in carbon-coated anatase might give possibilities to expand the applications of the photocatalysts ; for example, removing the pollutants in the water by adsorption during night and then decomposing them under solar light in daytime.

Here, the preparation and characterization of carbon-coated anatase photocatalysts were reviewed, mainly based on our results on a series of works, in the relation to their photocatalytic activity, which was studied for the decomposition of phenol (Ph, C_6H_5OH) and two azo dyes, methylene blue (MB, $C_{16}H_{18}ClN_3S$) and reactive black 5 (RB-5, $C_{26}H_{21}N_5O_{19}S_6Na$), and iminocastidine triacetate (IT, $C_{24}H_{53}N_7O_6$)^{4)-8), 10)-13)}. The photocatalytic activity of carbon-coated anatase was discussed in the relation to their crystallinity and adsorptivity. The merits and demerits of carbon coating were also discussed.

2. Preparation and Characterization of Carbon-Coated TiO₂

2.1 Preparation of carbon-coated TiO₂

It was found to be possible to cover the ceramic particle by carbon through a simple process, *i. e.*, the heat treatment of the mechanical mixtures of ceramics powder, including TiO₂, with a carbon precursor in various ratios at a high temperature above 500 °C in inert atmosphere. For the preparation of carbon-coated TiO₂, commercially available TiO₂ powder (ST-01 : Ishihara Sangyo Co., Ltd., Japan) was used as raw material, which consisted of the primary particles of about 7 nm from X-ray diffraction and of aggregated secondary particles about 60 nm from observation of SEM. In most cases, poly (vinyl chloride) (PVA) was used as carbon precursor. Hydroxyl propyl cellulose (HPC) and poly (ethylene terephthalate) (PET) were also used, especially to discuss on pore structure of carbon coated. Obtained samples were black in color and kept the property of fine particles of the pristine TiO₂, neither grinding nor cracking being necessary for their dispersion into water.

The samples prepared were shown by the sample codes according to the following rule ;

Starting sample*¹ and mixing ratio*² - temperature*³

where *¹ ST : only ST-01 and SP : mixture of ST-01 and PVA, *² Mixing ratio of ST-01 to PVA in mass, *³ Heat treatment temperature in °C for carbon coating. For example, **SP70-900** means the sample prepared from the mixture of ST-01 to PVA in mass ratio of 70/30 at 900 °C for 1 h, and **ST-500** means ST-01 heat-treated at 500 °C for 1 h without any carbon precursor mixed. The heat treatment temperature for carbon coating was selected at 400 ~ 1100 °C for 1 h and mixing ratio of TiO₂ (ST-01) to PVA was 50/50 to 95/5 in mass.

Amount of carbon coated on TiO₂ was determined by combustion in air at 800 °C in a TG apparatus. Crystal phases of TiO₂ formed by high temperature heat treatment were identified from powder X-ray diffraction pattern of the samples. Apparent BET surface area of

carbon-coated TiO₂ was determined from adsorption isotherm of nitrogen gas at 77 K in the relative pressure P/P_0 up to 0.3.

2.2 Characterization of carbon-coated TiO₂

Fig.1 reveals TEM images of carbon-coated TiO₂ samples SP90-900 and SP50-900, which have been prepared at 900 °C and contain 2 and 10 mass % carbon, respectively. On the TEM image, TiO₂ particles look dark because of low transparency for electron beam and carbons show relatively low contrast. Some of TiO₂ particles show a Moire pattern, because of high crystallinity due to 900 °C treatment. In the sample SP90-900 with 2 mass % carbon, carbon layers are very thin, but relatively thick in the sample SP50-900 with 10 mass % carbon.

SEM images of two samples, SP95-700 and SP50-700, which was coated by carbon at 700 °C and contained 2 and 16 mass % carbon, are shown in **Fig.2c**) and **d**), respectively, to compare with those of the pristine ST-01 and its 700 °C-treated (**Fig.2a**) and **b**), respectively). In spite of the heat treatment of 700 °C, it is proven that small particle size of 100 nm or less is kept after the carbon coating. After the heat treatment of the pristine ST-01 at 700 °C without mixing with PVA (ST-700), marked grain growth by sintering was observed as shown in **Fig.2b**).

Fig.1 Transmission electron micrographs of carbon-coated TiO₂ particles.

Fig.2 Scanning electron micrographs of pristine anatase powders and its carbon-coated ones.

Fig.3 Changes of X-ray diffraction pattern with heat treatment temperature on the mixture with the mass ratio ST-01/PVA of 50/50.

Fig.4 Dependences of apparent BET surface area on carbon content for 3 carbon precursors.

Changes in X-ray diffraction (XRD) patterns with heat treatment temperature are shown on the pristine ST-01 and on the mixture of ST-01/PVA = 50/50 in Fig.3a) and b), respectively. The pristine ST-01 has XRD pattern consisting of broad diffraction peaks, which can be attributed to anatase structure. This anatase phase started to transform to rutile phase by the heat-treatment at 700 °C, and completed at 900 °C. When this ST-01 was heat-treated with PVA in the ratio of 50/50, however, the transformation to rutile was retarded up to 900 °C. Even above 900 °C, rutile phase hardly increased and most of TiO₂ crystals existed as anatase phase even after 1100 °C treatment. Therefore, the transformation of anatase to rutile phase is suppressed by the carbon coating. Carbon is not seen on the XRD patterns of carbon-coated TiO₂, since coated layer of carbon has very low crystallinity.

On the samples prepared from the mixture of ST-01/PVA = 50/50 at 700 and 800 °C (SP50-700 and SP50-800) in Fig.3b), the diffraction lines of anatase phase are broad, revealing that crystallinity of anatase phase seems not to be improved. On the other hands, the diffraction lines of anatase phase in the samples heat-treatment above 900 °C, in which anatase transforms partly to rutile phase, become sharp, indicating the improvement in

crystallinity. For example, when the diffraction lines of around 39° in 2θ was paid attention, it was separated to three diffraction line of 103, 004, 112, through heat-treated above 900 °C. However, in the samples treated at the temperature of 800 °C or less, these three diffraction lines were broad and overlapped with each other, and so those peaks were observed as one diffraction line.

In Fig.3c), XRD patterns of the carbon-coated TiO₂ prepared from mixtures with different mixing ratio ST-01/PVA at 900 °C are compared. In the sample SP50-900, a trace of rutile phase is detected. In the sample SP90-900, diffraction peaks attributed to either anatase and rutile were detected, and in addition many small peaks are recognized, most of them being indexed by the phase Ti₄O₇, one of the reduced phases Ti_nO_{2n-1}, which is reasonably supposed to be formed through the reaction between TiO₂ and carbon coated¹⁴⁾.

2.3 Pore structure and adsorptivity of carbon layer coated

In order to discuss on the pore structure of carbon layer coated on TiO₂ (ST-01), PVA, HPC and PET were used as a carbon precursor with heat treatment at 700 ~ 900 °C to prepare carbon-coated TiO₂.

In Fig.4a), b) and c), apparent BET surface area measured on carbon-coated TiO₂ prepared from PVA, HPC and PET, respectively,

at different temperatures was shown by plotting against amount of carbon coated (carbon content). By increasing from 700 to 900 °C in heat-treatment temperature, BET surface area increased even at the identical carbon content. The apparent surface area increases with increasing amount of carbon coated, but tends to saturate. In comparison with three figures a), b) and c) in Fig.4, PET gives larger surface area and larger amount of carbon coated than PVA and HPC. This is due to the fact that carbonization yield of PET is much larger than those of PVA and HPC¹³⁾.

The pristine TiO₂(ST-01) had relatively large surface area as 300 m²/g, but after the heat treatment at 700 and 900 °C BET surface area decreased to 31 and 2 m²/g, respectively, due to grain growth, as shown in Fig.2b). BET surface area of the carbon layer coated was calculated from apparent BET surface area measured on carbon-coated TiO₂ was about 1000 m²/g by considering the amount of carbon coated and assuming BET surface area of TiO₂ of 30 m²/g because of the hindrance of grain growth of TiO₂.

By applying the same method to prepare carbon-coated MgO and isolating carbon from MgO by dissolving with dilute sulfuric acid, the carbons from PVA, HPC and PET were proven to be very porous¹⁵⁾.

In Fig.5a), b) and c), the saturated amount of adsorption

(adsorptivity) for MB, which was determined in MB solution of 2.54×10^{-4} mol/dm³ at room temperature by soaking enough period, was plotted against apparent BET surface area for the carbon-coated TiO₂ prepared at 700 ~ 900 °C from PVA, HPC and PET, respectively.

Adsorptivity for MB is roughly proportional to apparent BET surface area of carbon-coated TiO₂, in other words, strongly depends on the content of carbon in the catalysts. It has to be pointed out that there was not so much difference in adsorptivity among the catalysts prepared from three different carbon precursors in Figs.5a) to c).

3. Photocatalytic Activity of Carbon-Coated TiO₂

3.1 Optical diffuse reflectance spectra of carbon-coated TiO₂

Optical diffuse reflectance spectra of carbon-coated TiO₂ prepared at 900 °C with different mixing ratio to PVA are shown in Fig.6.

Optical adsorption by carbon-coated TiO₂ is generated over whole region of wavelength from ultra-violet to visible light. Absorption above 420 nm wavelength increases with decreasing

Fig.5 Dependences of adsorptivity of methylene blue on apparent BET surface area for the sample prepared from 3 different carbon precursors.

Fig.6 Diffuse optical absorption spectra of anatase (ST-01) and carbon-coated TiO₂ samples.

Fig.7 Changes in relative concentration c/c_0 of methylene blue (a), reactive black 5 (b), phenol (c) and iminocadine triacetate (d) in their solutions with irradiation time of UV rays on pristine ST-01 and carbon-coated TiO₂ prepared at 900 °C.

mixing ratio from 95 to 50, *i. e.*, increasing with carbon content, pristine ST-01 containing no carbon and having no absorption in the wavelength range above 420 nm. However, it was proven that the optical absorption edge near 360 nm attributed to anatase was clearly observed, even on carbon-coated TiO₂ samples. Therefore, optical diffuse reflectance spectra observed on carbon-coated TiO₂ is concluded to be a result of overlapping two spectra, one due to carbon coated on TiO₂ and the other due to anatase-type TiO₂, the latter being the origin for photocatalytic activity under UV irradiation observed on carbon-coated TiO₂.

3.2 Photodecomposition of various pollutants

MB, RB5, Ph and IT were selected as model pollutant materials. MB and RB-5 are azo-dyes. MB and Ph have been frequently selected as model pollutants in research on photocatalysts. IT is mainly used as a preventive medicine which has the therapeutic effect for the anthracnose as a disinfectant for the garden, of which removal has been desired in order to avoid the contamination of river water.

In the series of our works, it was aimed to evaluate photocatalytic activity and adsorptivity separately on carbon-coated TiO₂, because it sorbed a large amount of pollutants on the carbon layer. Before UV irradiation to decomposition, these sample powders were dipped in a high concentration solution of the pollutant for sufficient time in the dark, by mixing of catalyst with pollutant solution until the saturation in adsorption. From the decrease in concentration of the pollutant in the solution, saturated amount of adsorption of pollutant into carbon-coated TiO₂ samples (adsorptivity) was

determined. After the saturation of adsorption, photocatalyst powders were transferred into the solution with a low concentration, and then UV irradiation was started. Relative concentration of pollutant in the solution, c/c_0 , was measured by using either UV-Vis or HPLC as a function of UV irradiation time.

For all photocatalysts and pollutants used in the present work, the relation between $\ln(c/c_0)$ and irradiation time t could be approximated to be linear,

$$\ln(c/c_0) = -kt$$

and so the slope of the line observed, *i. e.*, the rate constant k , was determined as a measure of photocatalytic activity of each photocatalyst^{(10), (11)}.

Behaviors of the photodecomposition of MB, RB5, Ph and IT by using carbon-coated TiO₂ prepared with different mixing ratios ST-01/PVA at 900 °C are shown in **Fig.7**.

Since the saturation of adsorption was carried out in a high concentration solution the concentration of the solution increased in many samples in the initial stage of the irradiation, when those saturated sample powders were transferred into low concentration solution, and UV irradiation started, because of dissolution of pollutant molecules adsorbed in a high concentration solution. Therefore, the linear approximation to determine k was done by the exclusion of the part in which initial concentration increases. In most cases, therefore, the approximated line did not pass through $\ln(c/c_0) = 100\%$ at $t = 0$. However, the increase in the initial

concentration before UV irradiation was within 120 %, and so the effect of the substantial change in initial concentration to rate constant k seemed to be small.

It was not possible to compare the values of k determined in four different pollutant solutions on one sample directly, since the concentrations of the solutions were different and also irradiation conditions could not be exactly the same. Therefore, the effect of the carbon coating was discussed by comparing with the pristine ST-01 for each pollutant.

For MB, all carbon-coated TiO_2 photocatalysts prepared at 900 °C have higher k values than the pristine ST-01 (Fig.7a). For the decomposition of RB5, on the other hands, carbon-coated TiO_2 photocatalysts have much smaller k values than ST-01 (Fig.7b). Among the carbon-coated samples prepared at 900 °C, the sample SP70-900 has the highest k value, as in the case of MB. For the decomposition of Ph, the sample SP70-900 has almost the same value of k as ST-01 has. The decomposition of IT by TiO_2 photocatalysts, not only carbon-coated TiO_2 but also the pristine ST-01 without carbon coating, was much slower in comparison with those for other three pollutants, but carbon-coated TiO_2 photocatalysts had only a little smaller k values for ST-01.

3.3 Photocatalytic activity and crystallinity of TiO_2

The crystallinity of TiO_2 was reported to give a strong influence on its photocatalytic-activity, TiO_2 photocatalyst with high crystallinity of anatase phase showing high photocatalytic activity for the decomposition of pollutants in water^{(10), (12)}. The crystallinity of anatase phase was evaluated by the full width at half maximum intensity (FWHM) of 101 diffraction line of anatase phase without any correction on instrumental broadening, *i. e.*, apparent FWHM. In Fig.8a), rate constant k for the decomposition of MB was plotted against FWHM for carbon-coated TiO_2 photocatalysts prepared at 700 and 900 °C. In the samples prepared at 700 °C, which was shown to be a single phase of anatase, k values increases rapidly with the small decrease in FWHM. On the other hands, the samples

prepared at 900 °C show a maximum at about 0.6 ° of FWHM. The samples with FWHM of about 0.7 and 0.6 ° contained only TiO_2 of anatase phase, but in other samples with smaller FWHM, 0.5 and 0.23 °, anatase transformed partly to rutile phase, this being the reason why k value decreases in high FWHM side, above 0.6 °.

The k values for the decomposition of four kinds of pollutants was plotted against FWHM of 101 diffraction line of anatase for the samples prepared at 900 °C in Fig.8b). The k for each pollutant exhibits a maximum at around 0.6 ° in 2θ ($\text{CuK}\alpha$). Even though direct comparison among the k values measured for different pollutants was difficult due to experimental conditions, as pointed out before, it has to be pointed out that the dependences of k value, in other words, photocatalytic activity, on crystallinity of anatase photocatalyst is the same for different pollutants, a maximum activity being possible to have on TiO_2 with apparent FWHM of about 0.6 °, just before the transformation to rutile phase.

On carbon-coated TiO_2 photocatalysts, which were prepared from PVA, HPC and PET as a carbon precursor in the same process, a strong dependence of k value for the decomposition of MB on FWHM of 101 diffraction line of anatase phase were observed, as shown in Fig.9a). In this experiment, FWHM was calibrated on instrumental broadening of diffraction lines by using silicon powder standard, and so the maximum k value was observed at about 0.3 ° in Fig.9a), instead of 0.6 ° in Fig.8. A clear and strong dependence of the rate constant k , *i. e.*, photocatalytic activity, for MB decomposition on crystallinity of anatase phase was proved. The main reason for the rapid decrease in k value with decreasing FWHM below 0.3 ° can be understood to be the decrease in anatase content in TiO_2 , in other words, partial transformation of anatase to rutile, by comparing Fig.8a) to Fig.8b) where anatase fraction is plotted against FWHM of anatase.

Often crystallite size was 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

Fig.8 Dependences of rate constants k on full width at half maximum (FWHM) intensity of 101 diffraction line of anatase phase for four pollutants.

Fig.9 Dependences of rate constant k for methylene blue decomposition and amount of anatase phase on full width at half maximum (FWHM) intensity of anatase phase for a series of carbon-coated TiO₂ samples prepared from different carbon precursors.

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 might be suggested the presence of a large amount of lattice strain. Even after heat-treatment at 900 °C, the diffraction lines for carbon-coated anatase were broad⁴⁾, revealing no marked annealing in crystallinity.

On TiO₂ without carbon coating, similar relation between FWHM of anatase phase and rate constant k for the decomposition of MB was obtained^{13), 14)} and tried to evaluate crystallite size and lattice strain separately to discuss on the relations to rate constant k ¹⁵⁾.

3.4 Photocatalytic activity and carbon content

In **Fig.10**, the rate constant k for the decomposition of MB is plotted against carbon content for carbon-coated TiO₂ prepared from PVA at various temperatures. For the samples prepared at 700 and 800 °C, k decreases with increasing carbon content, but shows a maximum at about 4 and 9 mass % of carbon for the samples prepared at 850 and 900 °C, respectively. Although thickness of carbon layer coated on TiO₂ particles was difficult to be determined directly, it is reasonably supposed that the higher the amount of coated carbon is the thicker the carbon layer on TiO₂ is. Therefore, the decrease in k with increasing carbon content, which was observed even partly on the samples prepared at different temperatures is supposed to be due to the weakening of UV rays arriving on TiO₂ particles through carbon layer. With increasing heat treatment temperature, rate constant k increases, which is due to the improvement of crystallinity of anatase phase, as discussed in the previous section (**Fig.8a** and **9a**). However, beyond certain crystallinity improvement, the transformation of anatase to rutile phase occurs, as also shown in **Fig.9b**). This is the reason why the k value decreases at the region of low carbon content for the samples prepared at 850 and 900 °C, as anatase content in each sample is indicated in the figure. Therefore, the result shown in **Fig.10** suggests that the decomposition rate k observed on carbon-coated TiO₂

Fig.10 Dependences of rate constant k for methylene blue decomposition on carbon content for carbon-coated TiO₂ prepared at different temperatures.

photocatalysts is determined as a balance among different parameters, thickness of carbon layers coated, crystallinity of anatase and anatase content, etc.

3.5 Photocatalytic activity and adsorptivity

Adsorptivity of carbon-coated TiO₂ photocatalysts was determined on four pollutants, MB, RB5, Ph and IT, and discussed on the relations to apparent BET surface area. Adsorptivity of carbon-coated photocatalysts depends strongly on the adsorbate (*i. e.*, MB, RB5, Ph, IT), but also on the surface nature of carbon layer on TiO₂ particles. Amount of saturated adsorption (adsorptivity) for MB, RB5, Ph and IT on the carbon-coated TiO₂ was plotted against apparent BET surface area for carbon-coated TiO₂ prepared at 700 and 900 °C in **Fig.11a**) and **b**), respectively. Adsorptivity for each pollutants increases with increasing apparent BET surface area, but saturation tendency is observed above 140 m²/g on all pollutants. Adsorptivity of carbon-coated TiO₂ strongly depends on pollutant; MB is adsorbed in large amount but Ph and RB5 are in relatively small. When the molecular size was compared on these pollutants, molecular size does not govern the adsorption into

Fig.11 Saturated amount of adsorption against BET surface area of carbon layer of carbon-coated TiO_2 prepared at 700 and 900 $^{\circ}\text{C}$ for four pollutants.

Fig.12 Relations of rate constant for photodecomposition for four pollutants against adsorptivity on carbon-coated TiO_2 prepared at 700 and 900 $^{\circ}\text{C}$.

carbon, large sized MB (5×3 nm) being adsorbed in a large amount, but Ph with relatively small molecular size (about 0.8 nm) being not so much adsorbed.

In Fig.12, rate constant k for the decomposition of four pollutants is plotted against adsorptivity for each pollutant of carbon-coated TiO_2 photocatalysts prepared at 700 and 900 $^{\circ}\text{C}$.

These results of relation of rate constant and adsorptivity in 700 and 900 $^{\circ}\text{C}$, respectively show that the pollutant adsorbed in the larger amount into carbon-coated TiO_2 photocatalyst can be decomposed with the higher rate k , although the rate constant k for each pollutant is also determined by other factors, such as crystallinity and content of anatase through occurring from the different heat treatment condition.

4. Fixation and Cycling Performance of Carbon-Coated TiO_2

4.1 Cycling performance of powder photocatalysts dispersing in solution.

In order to check cyclic performance of carbon-coated TiO_2 photocatalysts, one of the samples SP70-900 in powder were repeatedly used for the decomposition of IT by dispersing in its solution. In Fig.13, the plots of logarithm of relative concentration of IT in the solution $\ln(c/c_0)$ vs. irradiation time t are shown for

Fig.13 Cyclic performance of carbon-coated TiO_2 , SP70-900, for the decomposition of IT.

1st and 2nd cycles of the use. The samples of photocatalyst were kept firstly in the dark for 200 hours to saturate the adsorption of IT in its solution with the initial concentration of 100 ppm and

then exposed to UV irradiation (1st cycle). After about 100 hours irradiation, the sample was separated from the test solution by filtering and then dispersed again into a virgin solution with 100 ppm concentration to follow the same process, 200 hours in the dark and then irradiation by UV (2nd cycle).

In the dark, relative concentration change before 2nd 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 2nd cycle, as fast as in the 1st cycle. Therefore, IT molecules in the solution were decomposed by the photoactivity of carbon-coated anatase. No marked difference in the rate constant k for the decomposition of IT, *i. e.*, the slope of the lines in **Fig.13**, between 1st and 2nd cycle was recognized. From these results, cyclic performance for the decomposition of IT and reusing of carbon-coated TiO₂ were proved. 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.

4.2 Fixation of carbon-coated TiO₂ in polymers and its cycling performance

Three acryl resin films were prepared, the film without any photocatalysts, that containing the original ST-01 and that containing carbon-coated sample SP50-700. In **Fig.14**, weight losses under UV irradiation with time of these three films are compared. The film containing ST-01 decreases its weight rapidly and reaches 39 % loss after 870 h, which is mainly due to the photocatalytic decomposition of the resin by TiO₂. However, the film containing SP50-700 shows only 5 % loss even after 870 h irradiation, which is almost the same as the acryl resin film without any photocatalysts. It is reasonably supposed to be due to the evaporation of remaining organic solvent during film casting. This reveals that carbon coating on TiO₂ particles works effectively to prevent the interaction with binder resins.

Carbon-coated TiO₂ photocatalysts prepared were fixed on one side of a double-sided adhesive organic tape and then the other side of the tape bonded to a glass plate. By using these carbon-coated TiO₂ fixed tapes, MB was decomposed by irradiating UV under circulating the MB solution. After the decomposition of MB was proceeded, the tape transferred into new MB solution and UV light irradiation was carried out. In **Fig.15**, the decomposition behaviors of MB were shown on 3 same kind tapes, on which the sample SP50-900 powder was fixed. It was proven that the carbon-coated TiO₂ could be resisted to the multiple uses.

Changes in k with repetitive use (cycling performance) were

Fig.14 Weight losses of three-acryl resin under UV irradiation.

Fig.15 Changes with recycling of carbon-coated TiO₂ fixed on organic tape.

Fig.16 Relations between logarithm of relative concentration $\ln(c/c_0)$ with irradiation time t for each repeated cycle for two carbon coated TiO_2 photocatalysts fixed on organic tape.

Fig.17 Dependence of rate constant k measure on different cyclic usages on carbon content of carbon coated TiO_2 prepared from PVA at 900°C .

measured in detail for different carbon-coated photocatalysts by using the same procedure, *i. e.*, fixing on one side of double-sided adhesive organic tapes. In **Fig.16**, the changes in logarithm of relative concentration $\ln(c/c_0)$ of MB with irradiation time t are shown on two samples SP70-900 and SP90-900. The relations between $\ln(c/c_0)$ and t for each cycle were approximated by straight line. In **Fig.17**, the k obtained from the slope of these straight lines for each cycle is plotted against carbon content of the samples used. Sample SP70-900, which has the highest k value for MB decomposition, as shown in **Fig.7a**), shows a little larger fluctuation of the experimental points, in comparison with other samples. However, the fluctuation in rate constant k is rather small and no definite tendency to change with cycling. Though the

fluctuation in k is a little different for the samples, it can be said to be in $\pm 0.05 \text{ h}^{-1}$, about 10-20 % fluctuation.

5. Conclusions

Carbon-coated anatase-type TiO_2 was prepared by the heat treatment of the powder mixtures of photocatalyst TiO_2 (ST-01) with thermoplastic carbon precursors, such as poly (vinyl alcohol), hydroxyl propyl cellulose, poly (ethylene terephthalate), etc., at a temperature between $700\text{--}900^\circ\text{C}$ for 1 h in inert atmosphere. Carbon layers formed on TiO_2 particles through the present process were confirmed to be porous and responsible for large apparent BET surface area measured on carbon-coated anatase, consequently for adsorptivity for different pollutants from their aqueous solution. Apparent rate constant k of the carbon-coated anatase for MB decomposition depended on the crystallinity of the anatase phase evaluated from the full width at half maximum intensity (FWHM) of 101 diffraction line of anatase phase.

Carbon layer coated on anatase particle was found to play different roles. It suppressed the phase transformation from anatase to rutile, which resulted in a high crystallinity of anatase phase and was advantageous to have high photoactivity for the photodecomposition of pollutants in aqueous solution. The thicker carbon layer gave the higher adsorptivity, but at the same time made UV rays arriving on the surface of anatase particle the weaker. The results of a series of our works^{(4)–(18)}, the merits and demerits of carbon coating on TiO_2 for photocatalyst applications are summarized as follows ;

Merits : 1) Suppression of phase transformation from anatase to rutile. 2) High crystallinity of anatase phase, which is preferable for water purification. 3) High adsorptivity for some pollutant. 4) Fixation by using organic binder because of interruption of direct contact between TiO_2 and organic binder. In addition, carbon coated can react with TiO_2 to form the reduced phases of TiO_2 , $\text{Ti}_n\text{O}_{2n-1}$, which were found to be active for visible light⁽¹⁹⁾.

Demerits : 1) Diminution of UV ray strength arriving on TiO₂ surface. 2) Strong dependence of apparent photoactivity on adsorptivity for the pollutants.

In order to have a high apparent rate constant k , *i. e.*, high photocatalytic activity, therefore, the balance among these different effects of carbon layers is strongly required. For the samples prepared at 850 °C shown in **Fig.10**, a good balance among these factors seemed to be obtained. The sample with carbon content of about 3.5 mass % gave the highest rate constant k , where the transformation to rutile was suppressed and carbon layer was thin enough to transmit UV rays to the surface of TiO₂ particle. Before this maximum in k , that is, less carbon content, less suppression of the transition of anatase to rutile was obtained and resulted in lower k value. After this maximum, that is, large carbon content, less transmission of UV rays was obtained and resulted in lower k value again. Therefore, the apparent rate constant k , photocatalytic activity, of carbon-coated anatase was determined as a balance between the suppression of the transition of anatase to rutile, resulting in high crystallinity of anatase and in small amount of rutile formed, and the decrease in UV rays reached on the surface of TiO₂, both of them being controlled by carbon layer.

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