

Carbon-Coated Anatase -Roles of carbon layer- カーボン被覆アナターゼ -カーボン層の役割

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Abstract Carbon-coated anatase-type TiO₂ was prepared by the heat treatment of the powder mixtures of photocatalyst TiO₂ (ST-01) with poly(vinyl alcohol) at a temperature between 700-900 °C for 1 h in Ar gas flow. Carbon layers formed on TiO₂ particles were confirmed to be porous and responsible for large apparent BET surface area measured on carbon-coated anatase, consequently for large amount of methylene blue (MB) adsorption from its aqueous solution. Apparent rate constant *k* of the samples 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. This rate constant *k* was found to be determined as a balance among the crystallinity improvement of anatase phase, the suppression of the phase transformation of anatase to much less active rutile and the decrease in UV rays reached on the surface of TiO₂, three of them being controlled by carbon layer.

1. INTRODUCTION

Activated carbon and photocatalytic TiO₂ anatase have given certain contributions for conservation of environment through adsorption and photodegradation of pollutants, respectively. Coupling of these two materials has been tried to hybridize two functions, adsorptivity and photoactivity, and also to create a new function. For composites of photocatalyst TiO₂ with carbon, three possibilities have been reported, TiO₂-mounted activated carbon, carbon-doped TiO₂ and carbon-coated TiO₂. TiO₂-mounted activated carbons were studied for the coupling of the photoactivity of anatase-type TiO₂ with the adsorptivity of activated carbon¹⁻⁵. However, a marked decrease in adsorptivity was also reported by mounting fine particles of TiO₂. Carbon-doped anatase-type TiO₂ was prepared and reported to have visible-light sensitivity⁶. Carbon-embedded and carbon-modified anatase photocatalysts were also prepared^{7,8}. Carbon-coated TiO₂ was firstly reported by our group⁹⁻¹⁶, which was completely different from TiO₂-mounted carbon in the positional relation between two components (TiO₂ and carbon). It was also different from carbon-doped TiO₂ in carbon content and color. The carbon-doped TiO₂ contained less than 1 mass% carbon and was yellowish, but carbon-coated TiO₂ had a carbon content more than 2 mass% and a black color. The technique for carbon coating of ceramic particles through a simple process to heat-treat a powder mixture of ceramics and thermoplastic carbon precursors has been applied for different purposes¹⁷⁻²⁸.

In the carbon-coated TiO₂, the pollutant molecules to be decomposed have to be adsorbed into the carbon layer that covers the TiO₂ particle, diffuse through the carbon layer to reach the surface of the photocatalyst TiO₂ and then be decomposed under UV irradiation. By the preparation of carbon-coated TiO₂, a coupling between photoactivity and adsorptivity was successfully achieved, as reported in our previous papers^{10,15}, some of them showing a higher activity than pristine TiO₂ without carbon coating. However, all characteristics, such as specific surface area, adsorptivity and photoactivity, determined for carbon-coated TiO₂ were apparent values, and so it was important to discuss them by separating the functions of each component. To determine the photoactivity by separating it from adsorptivity, we successfully employed the following procedure. Samples were saturated by the pollutant, such as methylene blue, before the measurement of photoactivity. In this procedure, the experimental points measured in the first 1 hour could not be used to determine the rate constant *k* for the decomposition of the pollutants, because some of the pollutants were coming out into the solution. By using MgO as the substrate ceramics, the carbon layers formed were found to be porous even though the precursors were thermoplastic polymers, such as poly(vinyl alcohol) and poly(ethylene terephthalate), and no activation process was employed²⁹. It was shown that the carbon layers coated on the ceramic particles were responsible for high apparent BET surface area and therefore for the large adsorptivity.

In the present work, the roles of carbon layers are discussed on the bases of the preparation and characterization of carbon-coated TiO₂ powders, and of their photoactivity measurements for methylene

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blue decomposition. The merits and demerits of carbon coating of photocatalysts were summarized.

2. EXPERIMENTAL

2.1 Carbon coating

The powder of poly(vinyl alcohol) (PVA, Unifika Co., Ltd.) was mixed with the powder of photocatalyst TiO_2 (ST-01, Ishihara Sangyo Co., Ltd.) in different ratios and then heat-treated on a tray of alumina (Al_2O_3) at various temperatures between 700 and 900 °C for 1 h in a flow of Ar. The pristine sample ST-01 was composed of a single phase of anatase with secondary particles of about 60 nm aggregated from the primary particles of about 7 nm, and had a relatively large BET surface area of about 300 m^2/g . The heating rate to the programmed temperature was 5 °C/min and the flow rate of Ar was 40 mL/min.

After heat treatment, the white powder of the pristine anatase changed its color to black, but its powdery nature looked no change. The appearances of two powders, before and after the carbon coating, are shown in Fig. 1.

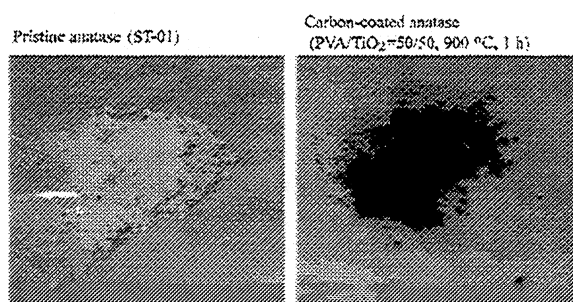


Fig. 1 Appearance of the powders before and after carbon coating.

2.2 Characterization

The carbon-coated TiO_2 thus prepared was characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface area. Crystalline phases in the samples were identified from XRD patterns with $\text{Cu K}\alpha$ radiation and the full width at half maximum intensity (FWHM) of the 101 diffraction line of anatase phase was used as a measure of its crystallinity, which was calibrated for the instrumental broadening by referring to standard silicon. BET surface area was determined on carbon-coated anatase from nitrogen adsorption isotherm up to a relative pressure of 0.3 at 77 K. The carbon content of the samples was determined from weight loss by burning at 800 °C in air. The relative content of anatase in TiO_2 , f_A , was determined from the diffraction intensities of the 101 line of anatase, $I_A(101)$, and the 110 line of rutile, $I_R(110)$, according to the following equation³⁰⁾,

$$f_A(101) = 1 - \{I_R(110)/[I_R(110) + 0.79I_A(101)]\}.$$

2.3 Adsorptivity

Adsorption of methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$, MB) in water was determined by the following procedure. A powder sample of 0.075 g was dispersed in 100 mL of an aqueous solution of MB with a concentration of 2.94×10^{-4} mol/L in the dark at room temperature. The concentration of MB was measured as a function of holding time from the absorbance at 664 nm wavelength of MB measured by a UV-Vis spectrophotometer. In most cases, the MB concentration became constant after 12 hours. Therefore, adsorptivity into each sample for MB (mol of MB per 1 g of carbon-coated TiO_2) was calculated from the decrease of concentration of MB in the solution after holding for 24 hours at room temperature in the dark.

2.4 Photocatalytic activity

In order to evaluate the photoactivity of the prepared samples, the decomposition behavior of MB in water was followed. Since carbon-coated TiO_2 samples had a large adsorption of MB, the sample powder was saturated by MB in a high concentration solution (2.94×10^{-4} mol/L) in the dark for 12 h and then transferred into the MB solution of 100 mL with a concentration of 2.94×10^{-5} mol/L. Powder samples of 0.075 g were dispersed under ultrasonic vibration for 5 min and then the UV irradiation started. For UV irradiation, two UV lamps of 20 W power were used at a distance of about 150 mm from the solution. By sampling 3 mL of solution after passing through a 0.2 μm membrane filter, the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 664 nm using a UV-Vis spectrophotometer whose calibration curve had been determined in advance. Since the plots of logarithm of relative concentration of MB, $\ln(c/c_0)$, in the solution against irradiation time, t , were approximately linear, as reported in our previous papers¹²⁻¹⁶⁾, the slope of the linear relation, *i.e.*, rate constant k , was determined for each sample.

3. RESULTS AND DISCUSSION

3.1 Formation of porous carbon on TiO_2 particles and its adsorptivity

The pristine TiO_2 had a large BET surface area as 300 m^2/g , but it was shown to give lower surface area as about 30 m^2/g after heat treatment at 700 °C and only 2 m^2/g after 900 °C because of grain growth by sintering¹²⁾. Carbon-coated TiO_2 was found to have relatively large surface area of more than 200 m^2/g even though carbon content was only 10 mass% after 900 °C treatment.

In Fig. 2a), apparent BET surface area measured on carbon-coated TiO_2 is plotted against carbon content as a function of heat treatment temperature. At 900 °C, apparent surface area increased rapidly from 50 m^2/g at the carbon content of 2 mass% to

220 m²/g at 11 mass% C. At 700 and 800 °C, a little smaller surface area was obtained and it tended to saturate at about 140 m²/g with increasing carbon content. By the 850 °C-treatment, an intermediate change in surface area was observed.

This apparent BET surface area was attributed to the formation of porous carbon layer on TiO₂ particles. By assuming that the substrate TiO₂ had a

surface area of 30 m²/g even after 900 °C treatment, even though this surface area was observed after 700 °C treatment without carbon coating because the sintering of TiO₂ particles was prevented, the surface area of carbon layer was calculated to be roughly 1500 m²/g for both carbon-coated TiO₂ with 2 and 11 mass% carbon content.

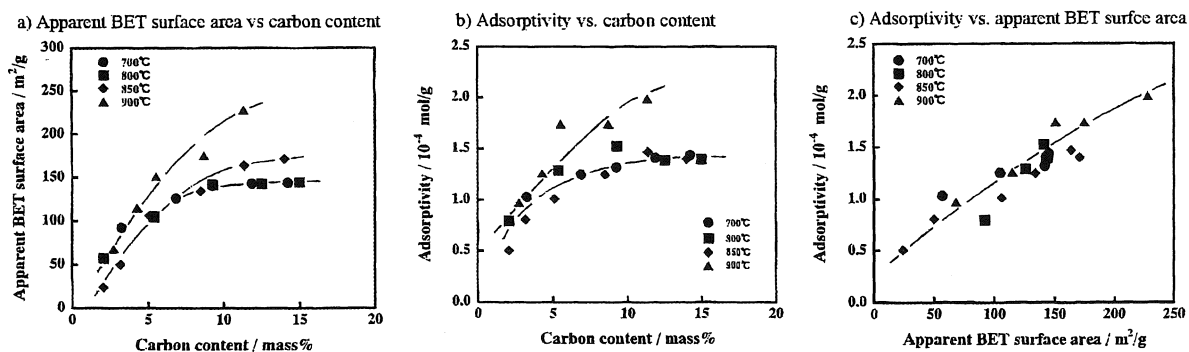


Fig. 2 Relations among apparent BET surface area, adsorptivity for methylene blue and carbon content for carbon-coated TiO₂.

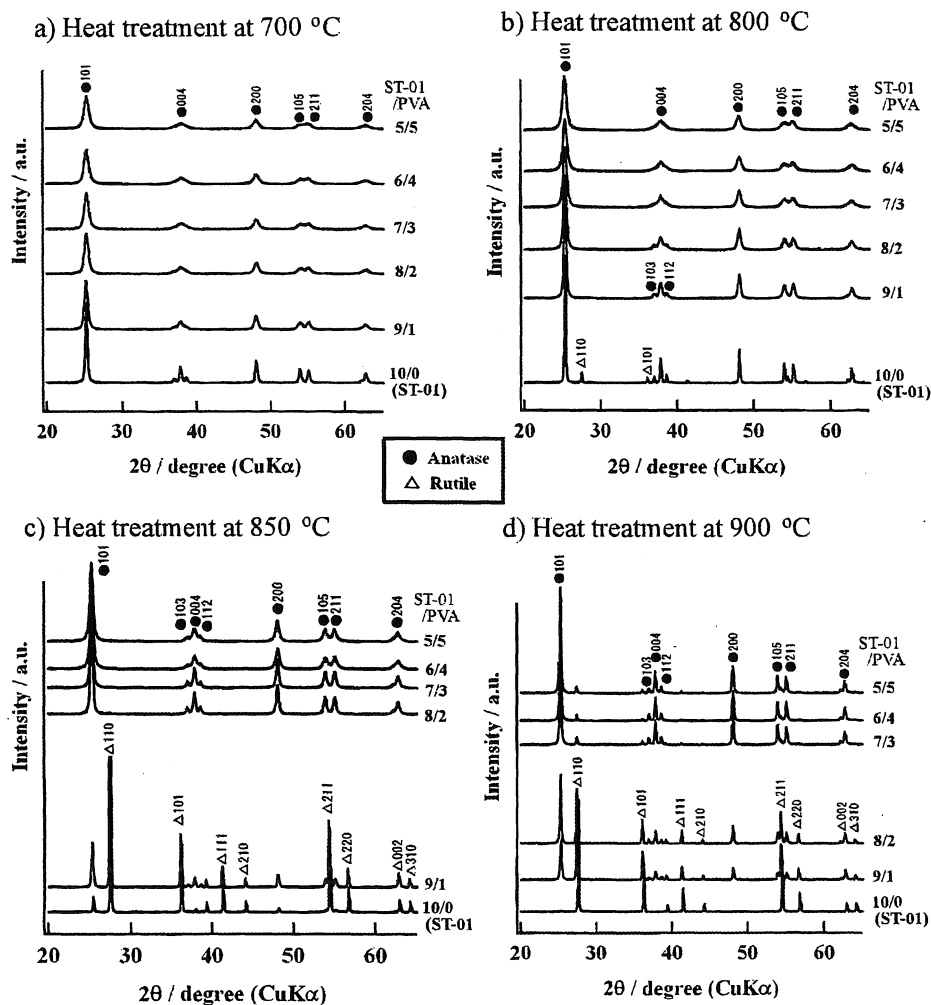


Fig. 3 Changes in X-ray diffraction pattern with mixing ratio of TiO₂/PVA and heat-treatment temperature.

In Fig. 2b), adsorptivity for MB is plotted against carbon content for carbon-coated TiO₂ prepared at different temperatures. Even though the experimental points are scattered, the dependences of adsorptivity is very similar to that of apparent BET surface area shown in Fig. 2a). Therefore, adsorptivity is re-plotted against apparent BET surface area in Fig. 2c). In the present carbon-coated TiO₂, adsorptivity for MB is almost linearly related to apparent BET surface area, for which carbon layer was mainly responsible, as discussed above.

The results shown in Fig. 2 show that pore structure of carbon layer formed on the particles of TiO₂ depends on heat treatment temperature, but adsorptivity for MB is closely related to apparent BET surface area, irrespective to heat treatment temperature. The same results were obtained on the carbon layers formed on TiO₂ particles from other precursors, hydroxyl propyl cellulose and poly(ethylene terephthalate), and the changes of BET surface area with heat treatment temperature and carbon content were discussed in the relation to carbonization behaviors of each precursors³³⁾. Highly microporous nature of carbon layer formed from PVA through the same procedure was demonstrated through isolating carbon from MgO substrate by dissolution^{29,34)}.

3.2 Suppression of phase transformation of anatase to rutile

In Fig. 3, X-ray diffraction patterns are shown on carbon-coated TiO₂ at four different temperatures. The pristine ST-01 (ST-01/PVA=10/0) started to transfer from anatase to rutile already at 800 °C and changed to a single phase of rutile with high crystallinity after the heat treatment at 900 °C. By mixing only 10 and 20 mass% PVA (9/1 and 8/2), however, the transformation to rutile was suppressed up to 850 and 900 °C, respectively. At 800 °C, crystallinity of anatase phase was high, as revealed by clear separation among diffraction lines of 103, 004 and 112. By the increase in PVA ratio (7/3, 6/4 and 5/5), only a small amount of rutile was detected even after 900 °C treatment.

Fig. 3 shows also that crystallinity improvement with heat treatment temperature depends strongly on mixing ration of ST-01/PVA. Carbon-coated TiO₂ prepared from the mixture of ST-01/PVA= 9/1, which had the smallest carbon content, showed the separation of 101, 004 and 112 diffraction lines already at 800 °C, but this diffraction line separation was observed only after the heat treatment at 900 °C on the carbon-coated TiO₂ from 5/5 mixture. which contained the largest amount of carb. After the diffraction lines sharpened, *i.e.*, crystallinity of anatase phase was improved, the phase transformation to rutile seemed to occur.

In Fig. 4, anatase content f_A is plotted against carbon content after heat treatment at different temperatures. Transformation to rutile strongly de-

pends on carbon content, as well as heat treatment temperature. Below 800 °C, a small amount of carbon coated was sufficient for the depression of the phase transformation, though it started without carbon coating (in the case of pristine ST-01) already at 800 °C (Fig. 3b). At 850 °C, the transformation was accelerated, but the carbon coating above 5 mass% could hinder the transformation completely. At 900 °C, a small amount of rutile, about 5 mass%, was formed even though the samples contained more than 5 mass% carbon, which might be due to an inhomogeneity of carbon coating. The rapid decrease in f_A with decreasing carbon content below 5 mass% suggests that the carbon content above 5 mass% is efficient for the suppression of phase transformation.

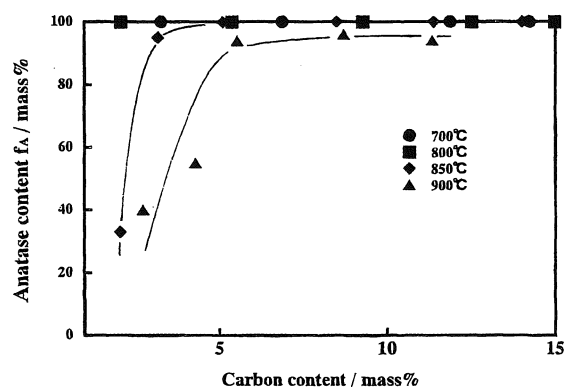


Fig. 4 Dependence of anatase content f_A on carbon content of carbon-coated TiO₂.

3.3 Photoactivity for methylene blue decomposition

In order to evaluate the rate constant for photodecomposition of methylene blue (MB), adsorption of MB by porous carbon layer on TiO₂ particles was saturated before UV ray irradiation. Since adsorption of MB by carbon was so high that relatively high concentration of MB solution (2.94×10^{-4} mol/L) had to be used and the sample was transferred into less concentric solution (2.94×10^{-5} ml/L) after saturation, the concentration of MB in the solution usually increase by ultrasonic dispersion and UV irradiation due to the partial dissolution of MB adsorbed into carbon layer in advance. Therefore, MB concentration increased in the very beginning of UV irradiation, but it did not become over 1.5 times. In Fig. 5, relative concentration of MB remained in the solution c/c_0 is plotted in logarithmic scale against irradiation time t for the samples prepared at 800 and 850 °C, for examples. The linear relation between $\ln(c/c_0)$ and t was approximated above 1 h irradiation and so the slope of the line, *i.e.*, rate constant k for photodecomposition of MB, was determined.

The samples heat-treated at 800 °C, which were composed of a single phase of anatase, showed a strong dependence of rate constant k on mixing ratio of ST-01/PVA, in other words, on carbon content, the

larger carbon content giving the smaller k . On the samples prepared at 850 °C, however, k for the sample with ST-01/PVA of 8/2, which was a single phase of anatase with high crystallinity, was much higher than that with 9/1, which consisted of two phases, anatase and rutile.

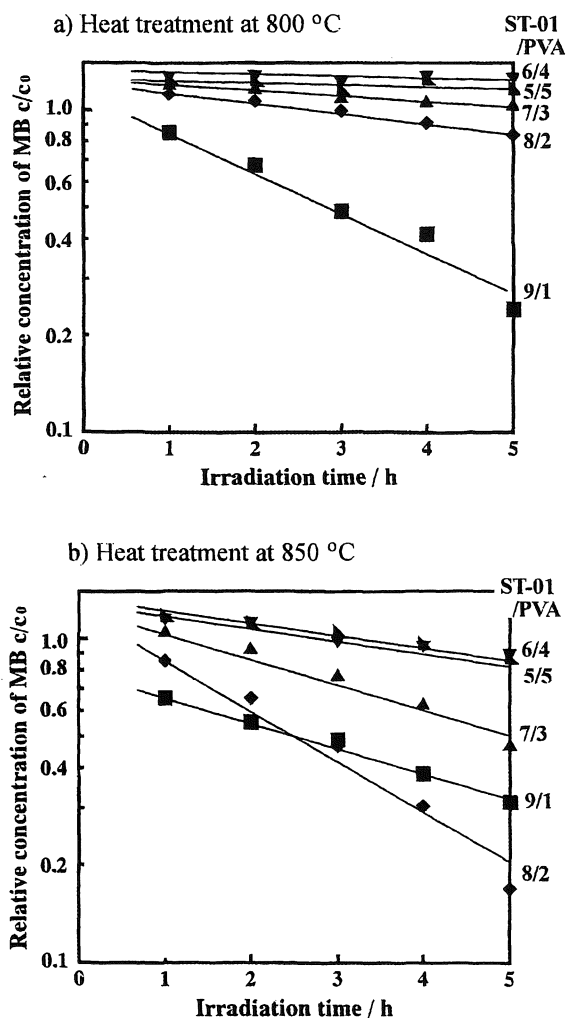


Fig. 5 Changes in logarithmic relative concentration of methylene blue remained in the solution $\ln(c/c_0)$ with irradiation time t of UV rays.

3.4 Dependence of rate constant for MB decomposition on crystallinity of anatase

In Fig. 6a) and b), the rate constant k for MB decomposition and anatase content f_A measured on carbon-coated TiO_2 are plotted against full width at half maximum intensity (FWHM) of 101 diffraction line of anatase phase of TiO_2 , respectively. Rate constant k shows a maximum around 0.3 ° in FWHM. Similar dependences of rate constant k on FWHM were observed on anatase powders prepared by sol-gel method and annealed at different temperatures^{31,32}, and also on carbon-coated TiO_2 for different pollutants¹⁴⁻¹⁶. The rapid decrease in f_A below the FWHM of 0.3 ° in Fig. 6b) shows clearly that the main reason why the rate constant k decreases below

0.3 ° (Fig. 6a) is the decrease in the content of photoactive anatase phase f_A . On the region of larger FWHM, where no rutile phase was formed, k increases with decreasing FWHM, in other words, with improvement in crystallinity of anatase.

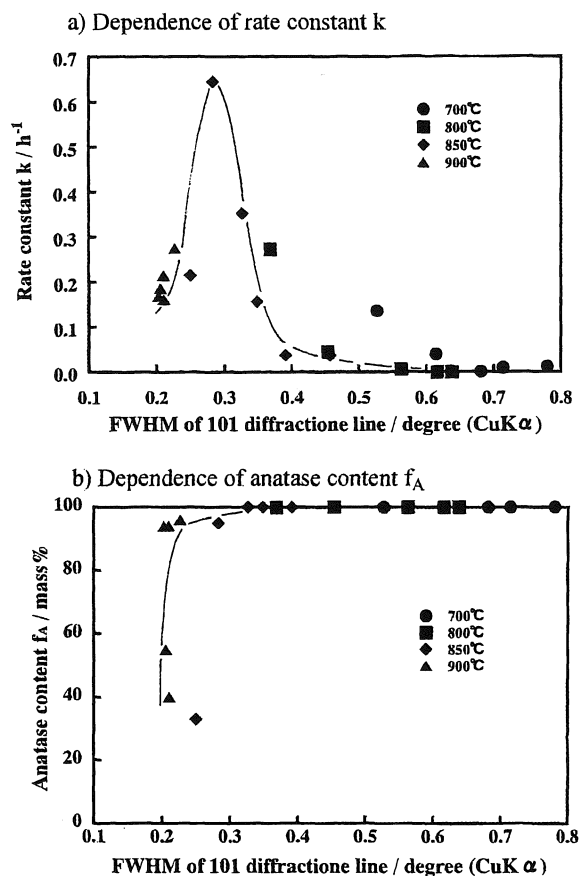


Fig. 6 Dependences of rate constant k for MB decomposition and anatase content f_A on full width at half maximum intensity (FWHM) of 101 diffraction line of anatase phase for carbon-coated TiO_2 prepared at different temperatures.

3.5 Dependence of rate constant for MB decomposition on carbon content

On the case of carbon-coated TiO_2 photocatalysts, the pollutant molecules has firstly to be adsorbed on carbon and then to diffuse to the surface of TiO_2 particle in order to be decomposed. In Fig. 7, rate constant k for MB decomposition is plotted against carbon content of the samples prepared at different temperatures. For the samples partially transformed to rutile, anatase content f_A was indicated.

On the samples prepared at 700 and 800 °C, which consisted of a single phase of anatase, rate constant k decreased with increasing carbon content. As shown in Fig. 2b), adsorptivity of the sample increased with increasing carbon content, showing a tendency to saturate and a dependence on heat treatment temperature. Therefore, the rate constant k

seems not to depend on the adsorption of MB of the carbon-coated samples. The samples prepared at 850 °C showed a maximum at a carbon content of about 3.5 mass%, but the sample with a low carbon content of 2 mass% had much lower k and also small f_A . On the samples prepared at 900 °C, the maximum in k shifted to a higher carbon content side and became smaller. Small k values on the samples with low carbon content are reasonably supposed to be due to small f_A , as discussed above.

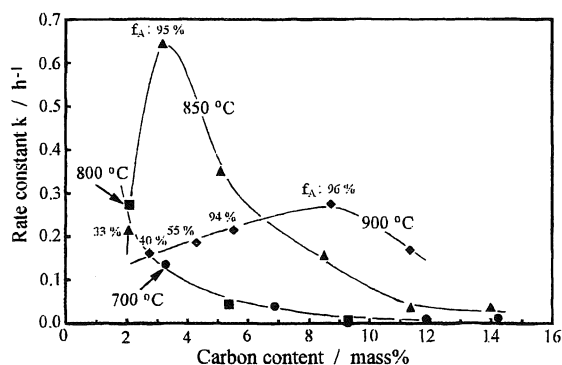


Fig. 7 Dependences of rate constant k for MB decomposition on carbon content for carbon-coated TiO_2 prepared from PVA at different temperatures.

With the increase in carbon content, the thickness of carbon layer coated on TiO_2 particle was reasonably supposed to increase and, as a consequence, the UV rays arriving on the surface of TiO_2 particle through carbon layer was weakened. Therefore, the diminution of UV ray strength arriving on TiO_2 particles seems to be principal reason for the decrease in k with increasing carbon content, which were observed on the samples prepared at 700 and 800 °C, and also those at 850 and 900 °C on high carbon content side, because TiO_2 in these samples was a single phase of anatase. The diffusion rate of pollutant molecules through carbon layer may also influence on photodecomposition rate. In the case of MB, however, it was supposed not to be determining factor because of large and rapid adsorption of MB into carbon-coated TiO_2 . With increasing heat treatment temperature from 800 to 850 °C, the crystallinity of anatase phase was improved and so photoactivity was enhanced, but also the phase transformation from anatase to rutile was accelerated, more markedly in the small carbon content side, resulting in the decrease in low carbon content side.

4. CONCLUDING REMARKS

Carbon-coated anatase-type TiO_2 was prepared by the heat treatment of the powder mixtures of photocatalyst TiO_2 (ST-01) with poly(vinyl alcohol) at a temperature between 700-900 °C for 1 h in Ar gas flow. 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 large adsorptivity for methylene blue (MB) from its aqueous solution. Apparent rate constant k of the samples 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 methylene blue 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.

On the bases of the present results, combining the results of our previous works^{10-16,33}, 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 pollutants. In addition, carbon layer coated on TiO_2 particles interrupts the direct contact between TiO_2 and solid organics, which works as a binder, and so 4) the carbon-coated TiO_2 particles were able to be fixed by using an organic binder¹⁰. 5) 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^{35,36}.

Demerits : 1) Diminution of UV strength arriving on TiO_2 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 photodecomposition rate, therefore, the balance among these different effects of carbon layers is strongly required. For the samples prepared at 850 °C in the present work, a good balance among these factors seemed to be obtained, as shown in Fig. 7. The sample with carbon content of about 3.5 mass% gave the highest rate constant k in the present work, where the transition to rutile was suppressed and carbon layer was thin enough to transmit UV rays to the surface of TiO_2 particle. Before this maximum in k less suppression of the transition of anatase to rutile was obtained because of less carbon coating. After this maximum less transmission of UV rays was obtained because of thick carbon coating. At 900 °C, the transition to rutile was accelerated and resulted in smaller k -values. At low temperatures as 700 and 800 °C, the crystallinity of anatase phase was not improved enough to get a high efficiency for the decomposition of pollutants in aqueous solutions. Carbon coating suppressed the

transition of anatase to rutile, but occurred when the crystallinity was improved to certain level, up to about 0.3 ° in FWHM of 101 diffraction line of anatase. The apparent rate constant k was determined as a balance between the suppression of the transition of anatase to rutile and the decrease in UV rays reached on the surface of TiO₂, both of them being controlled by carbon layer.

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