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Hybridization of adsorptivity with photocatalytic activity—carbon-coated anatase

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Abstract

Carbon-coated anatase catalysts were prepared from poly(vinyl alcohol) (PVA) and TiO_2 of anatase structure. Powders of PVA and commercial TiO_2 (ST-01) were mixed with different mass ratios and were heated at 700 and 900 °C under nitrogen. Such prepared catalysts were tested for adsorption and decomposition of two different dyes: methylene blue (MB) and Reactive Black 5 (RB5). Photoactivities of carbon-coated anatase catalysts were compared with ST-01. Carbon coating anatase suppressed anatase transformation to rutile at high temperatures. It was experimentally proved that this suppression appeared in samples with carbon content above 5 mass%. The crystalline structure of anatase was improved in catalysts heated at 900 °C. Although the sintering of anatase crystals was depressed by the carbon layer, the BET surface area of catalysts decreased, but not so much as it was observed in ST-01 heated at 700 °C. Adsorption of both dyes, MB and RB5 on carbon-coated samples was much more higher than on the original ST-01 and that heated at 700 °C. MB photodecomposition was much more higher on carbon-coated TiO_2 catalysts than on ST-01. But Reactive Black 5 was decomposed faster on ST-01 than on carbon-coated TiO_2. It can be explained by different mechanism of photodecomposition. Surface diffusion of adsorbed species through the carbon layer slowed down the rate of decomposition. High crystalline structure of anatase seems to be important in the photodecomposition process.

Keywords: Carbon-coated TiO_2; Adsorption; Photocatalytic properties; Methylene blue; Reactive Black 5

1. Introduction

Anatase-type TiO_2 has been interesting semiconductor because of its high photocatalytic activity [1–8]. Anatase transforms to rutile at high temperatures of heat treatment, which is not convenient, because of poor activity of rutile phase in most applications. This transformation temperature was reported to depend strongly on the preparation conditions of TiO_2 crystals [9]. It was already reported in our previous papers [10–13], that carbon coating TiO_2 particles can stabilize anatase structure and can increase adsorption of methylene blue on the catalyst surface without reduction of photocatalytic activity. Even higher photoactivity for methylene blue decomposition was observed on some carbon-coated TiO_2 catalysts. The procedure of carbon coating was very simple, mixing of powder TiO_2 with a raw carbon precursor, such as poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA), etc., and heating at high temperatures such as 700 and 900 °C for 1 h under nitrogen.

This procedure of carbon coating was applied on some ceramics, such as different aluminum oxides, magnesium oxide, titanium oxide, different iron oxides, nickel oxide, natural graphite, ceramic tiles [14–20], and aluminum plate [18,19]. Oxides particles were covered by the thin layer of carbon. Their color turned to black for the proper mixing ratio of carbon precursor to metal oxide used [14]. In the cases of transition metals such as Fe and Ni, their oxides were reduced to metals through the interaction with carbon, resulting in carbon-coated metal particles. By this catalytic formation of metals at temperatures of 900–1100 °C graphite crystals were formed [15–17]. Carbon coating of natural graphite flakes was found to improve the anodic performance in lithium ion rechargeable batteries [20]. Carbon coating

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of anatase-type TiO_2 has many advantages for the photocatalytic process, as mentioned above [10–13]. High resistance for the chemical corrosion tried to be obtained by carbon coating of ceramic tiles and aluminum plates [21,18,19]. In those experiments, different interactions between coated carbon and substrate ceramic particles, including the penetration of carbon into pores of γ-Al_2O_3 [14], were observed. A partial reduction of TiO_2 was detected from X-ray diffraction (XRD) analysis, but detailed structure and its photoactivity could not be determined in the previous work [11].

In present paper carbon-coated anatase catalysts were prepared and characterized by XRD, SEM, TEM, BET, and optical absorption spectroscopy. Kinetic studies of adsorption and photodecomposition of methylene blue (MB) and Reactive Black 5 (RB5) were performed. Hybridization of photocatalytic activity of anatase with adsorptivity of carbon was discussed.

2. Experimental

2.1. Carbon coating of TiO_2 particles

Carbon coating of TiO_2 was performed by mixing of a commercially available TiO_2 of anatase structure (ST-01, Ishihara-Sangyo Co. Ltd) with poly(vinyl alcohol) (Nippon Synthetic Chem. Ind. Co. Ltd.), in different mass ratios: 50/50, 70/30, 80/20, 90/10, and 95/5, respectively. After mixing the powders were heated at 700 and 900 °C for 1 h in nitrogen gas. The samples were heated with 10 °C/min heating rate and 100 mL/·min flow of nitrogen gas. Determined average size of ST-01 particles was 7 nm by XRD and 60 nm by SEM (aggregated particles). Average polymerization degree of PVA carbon precursor used was 2000 and particle size below 850 μm. The amount of carbon coated was determined from the weight loss of carbon-coated TiO_2 catalysts during heating at 1000 °C in air, due to the burning off the carbon. The original ST-01 was also heated at 700 and 900 °C.

The preparation conditions and characteristics of prepared samples are listed in Table 1.

2.2. Adsorption and photodecomposition of methylene blue

Samples of 0.021 g were dispersed into 40 mL of methylene blue solution (MB, $C_{16}H_{18}N_3S$, reagent grade) with the concentration of 2.94×10^{-4} mol/L and were stirred in the dark. Blue color of the solution was fading gradually with time due to the adsorption of MB on the catalyst surface. The pH value of the MB solution was kept around 6–7.

After saturation with adsorption, samples were taking to the new MB solution (2.94×10^{-5} mol/L) and were stirred under UV irradiation. Measured power flux of reactor was 1 mW/cm^2.

2.3. Adsorption and photodecomposition of Reactive Black 5

Firstly adsorption capacity for RB5 was determined on ST-01 and carbon-coated catalysts. 0.075 g of each catalyst was placed into 100 ml of RB5 solution with concentration of 0.05 g/L (5.32×10^{-4} mol/L). Adsorption was carried out in a dark, under magnetic stirring for 3 h, until saturation. After estimation of adsorption capacity of catalysts, combined process of adsorption and photodecomposition was performed. Different initial concentrations for each catalyst were used, process of adsorption was carried out again for 3 h. After adsorption the concentration of RB solution was around 0.01 g/L (1.06×10^{-4} mol/L). Then UV lamp was switched on and the process of photodecomposition was measured. Photodecomposition was conducted in the reactor equipped with 3 black-light blue fluorescent lamp GE/HITACHI FL20S BL B of 20 W power each one. This lamp emits the light in the wavelength range of 300–415 nm with a maximum at 352 nm. Measured irradiation power flux of UV rays inside reactor was 1.8 mW/cm^2.

Table 1
Carbon-coated anatase prepared

Sample code	HTT (°C)	TiO_2 (mass%)	Carbon coated (mass%)	Phases[a] (XRD)	Specific surface area (m^2/g)	Rate constant k of MB decomposition (h^{-1})	Rate constant k of RB5 decomposition (h^{-1})
ST-01		100	0	A (broad)	300	0.38	9.2
ST-01-700	700	100	0	A + R	30	0.38	–
ST-01-900	900	100	0	R	2	–	–
SP50-700	700	50	14.6	A (broad)	130	0.15	0.11
SP70-700	700	70	9	A (broad)	120	0.26	0.09
SP90-700	700	90	5	A (broad)	60	0.55	–
SP95-700	700	95	2	A + R	40	1.1	0.23
SP50-900	900	50	10	A	170	0.49	0.28
SP70-900	900	70	8	A	130	1.3	0.57
SP80-900	900	80	5	A + N	100	1.1	0.41
SP90-900	900	90	2	A + N	50	0.59	0.11

[a] A: anatase, R: rutile and N: Ti_4O_7 phase.

2.4. Analytical methods

The measurements of MB and RB5 concentrations remained in the solution was followed by sampling of 3 mL solution at an appropriate time interval and measuring the optical absorbance at a wavelength of 664 and 597 nm which have been attributed to absorption maximum of MB and RB5, respectively. Calculation of dyes concentration was followed by the measurement of absorbance, with using calibration curve.

X-ray diffraction patterns were measured with Ni-filtered Cu Kα radiation and scanning speed of 2°/min. BET surface area was measured from adsorption isotherm of nitrogen at 77 K. Optical absorption spectra of samples were measured in UV-Vis spectrophotometer at the wavelength of 220–850 nm by using diffuse scattering method.

3. Results and discussion

3.1. Characteristics of carbon-coated anatase

Carbon-coated TiO_2 catalysts looked black, due to the carbonization of PVA. The original ST-01 was kept white after heating at the same temperature. SEM micrographs of samples, ST-01, ST-01-700, SP50-700, SP95-700, SP50-900, and SP90-900 are shown in Fig. 1. In the original ST-01 aggregated particles with the size of around 60 nm are observed (Fig. 1a). After heating at 700 °C most of the ST-01 particles were sintered with each other and became larger than 1000 nm, though a small amount of fine particles still remained. In SP50-700 and SP95-700 samples, the particles size observed under SEM was 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 d, respectively. In samples heated at 900 °C the sintering of the particles was also retarded, but only in the samples with high content of carbon, for sample with the low content of carbon, i.e. SP90-900, big sintered particles are observed together with small ones, as presented in Fig. 1e.

In Fig. 2. TEM photos of SP50-900 sample are shown. The particles size is about 20 nm in a diameter, higher than the original ST-01, because of the crystal growth during heat treatment at high temperature. Prepared TiO_2 particles are covered by the carbon layer, however, it is pretty difficult to observe it on these photos, because this layer should be very thin according to the low content of carbon in carbon-coated TiO_2 catalyst.

Carbon content in carbon-coated TiO_2 samples decreases with decreasing of PVA/TiO_2 mixing ratio and with increasing the temperature of heat treatment.

In Fig. 3a XRD patterns of samples heated at 700 °C are shown. Anatase structure is kept almost in all carbon-coated TiO_2. Only in the sample with the smallest content of

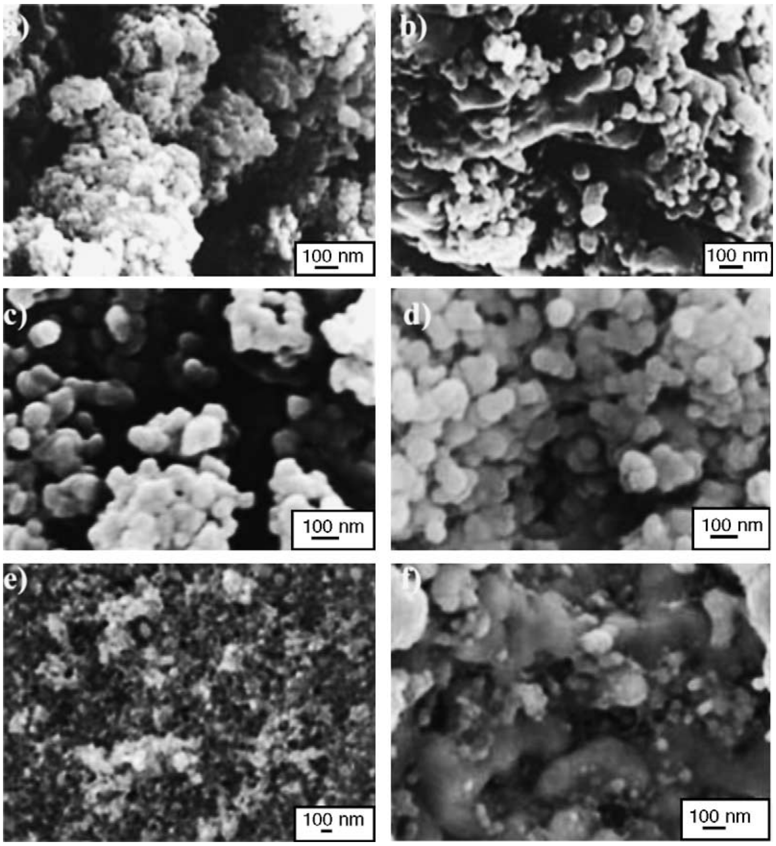


Fig. 1. SEM images of samples: (a) ST-01, (b) ST-01-700, (c) SP50-700, (d) SP95-700, (e) SP50-900, and (f) SP90-900.

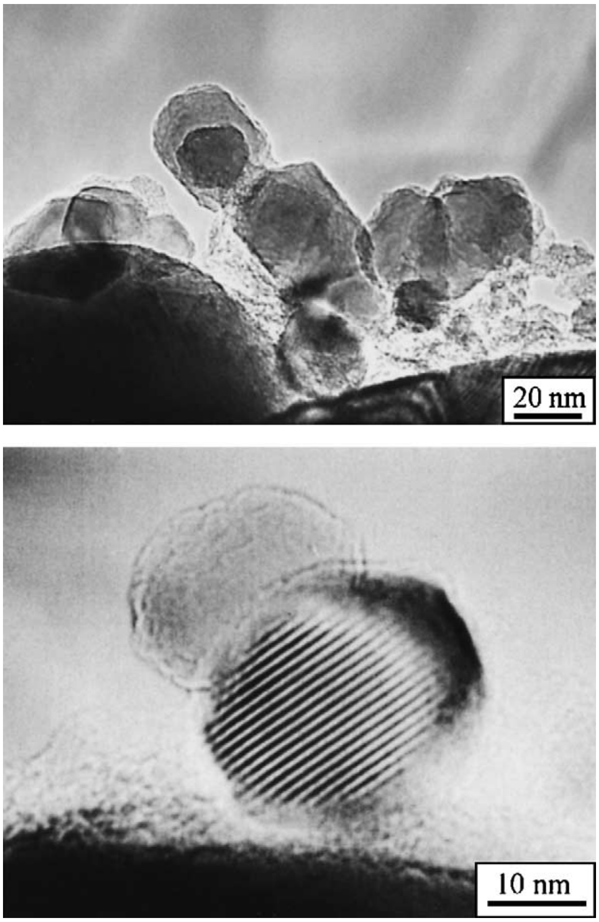


Fig. 2. TEM images of SP50-900 sample.

carbon, SP95-700, anatase transformed partly to rutile, as it happened in the original ST-01 without carbon coating.

In Fig. 3b XRD patterns of samples heated at 900 °C are presented. Anatase peak became sharper in those samples, but for TiO_2/PVA mixing ratio above 80/20, a new Ti_4O_7 phase appeared, and was clearly observed in SP90-900 sample. From these studies it was proved that carbon coated of TiO_2 particles in the amount above 5 mass% can suppress the transformation of anatase to rutile phase at high temperatures, and also at 900 °C anatase phase can be reduced to Ti_4O_7 by interaction with carbon in nitrogen atmosphere.

The crystalline structure of ST-01 has been improved by heating at 900 °C, what has been indicated by the sharpening of all diffraction lines on XRD pattern (Fig. 3b), especially through the separation of 1 0 3, 0 0 4, and 1 1 2 diffraction peaks at around 38° in 2θ scale. Improvement in the crystallinity was not so pronounced in the carbon-coated TiO_2 heated at 700 °C, broad diffraction lines and no separation among three diffraction peaks mentioned above occurred (Fig. 3a). This XRD measurement is in good agreement with SEM observations that showed sintering of TiO_2 particles by heating at high temperatures. Samples heated at 900 °C had better crystalline structure of anatase than the original ST-01, but at the same time Ti_4O_7 phase appeared, as it was shown in Fig. 3b.

It can be observed, that with decreasing of carbon content in the obtained samples, the crystalline structure of anatase has been improved. The samples coated by less than 5 mass% of carbon (SP90-700, SP95-700, SP90-900, and SP80-900) contained additional phases, rutile, and/or Ti_4O_7, and at the same time sharp peak of anatase. In the samples coated by more than 5 mass% of carbon, the principal phase was anatase. These studies are in a good correlation with our previous results for that the minimal content of carbon in TiO_2-coated carbon samples for suppression of phase transformation from anatase to rutile was around 5 mass% [22].

Carbon peaks could not be observed from XRD diffraction patterns because of the low content of carbon in the catalysts and also its low crystallinity.

Values of BET surface area of samples are shown in Table 1. The original ST-01 has rather high surface area of about 300 m^2/g, but after heating up to 700 °C BET surface area of ST-01 decreased to 30 m^2/g, and after 900 °C, to 2 m^2/g. It was caused by the sintering of TiO_2 particles and transformation of anatase to rutile. The surface area of carbon-coated TiO_2 decreased also after heating at 700 °C and was below 130 m^2/g. In Fig. 4 BET surface area is plotted against carbon content of samples. On carbon-coated TiO_2 samples, carbon layer on anatase particles reasonably contributes in BET surface area, even though its content is not so high. Sintering of TiO_2 particles was avoided by carbon coating and also anatase transformation to rutile was suppressed, so the original surface area of ST-01 was not reduced significantly in carbon-coated TiO_2 samples than it was in ST-01 without carbon coating. Reduction of BET surface area of carbon-coated TiO_2 catalysts was also caused by the growth of crystals. However, it is not possible to measure the surface area of carbon and TiO_2 in carbon-coated TiO_2 samples separately.

3.2. Optical absorption spectra

In Fig. 5 the optical absorption spectra of carbon-coated anatase samples are compared with the original ST-01. ST-01 of a single anatase phase shows a clear absorption edge at around 320 nm, as reported in many papers on anatase samples, and no absorption in visible light region above 380 nm is observed. In carbon-coated TiO_2 samples absorption of visible light is observed, such as the pure carbon shows absorption in the whole range of wavelength. Absorption spectra of carbon-coated samples may be understood to comprise of overlapping absorption spectrum of carbon and anatase. For SP95-700 sample absorption of light in the whole range of wavelength is rather small (because of a small amount of carbon), and the absorption edge due to anatase is obviously detected, though the accurate calculation of the band gap energy is pretty difficult. With increasing of carbon content in samples, absorption of a visible light due to carbon becomes more pronounced

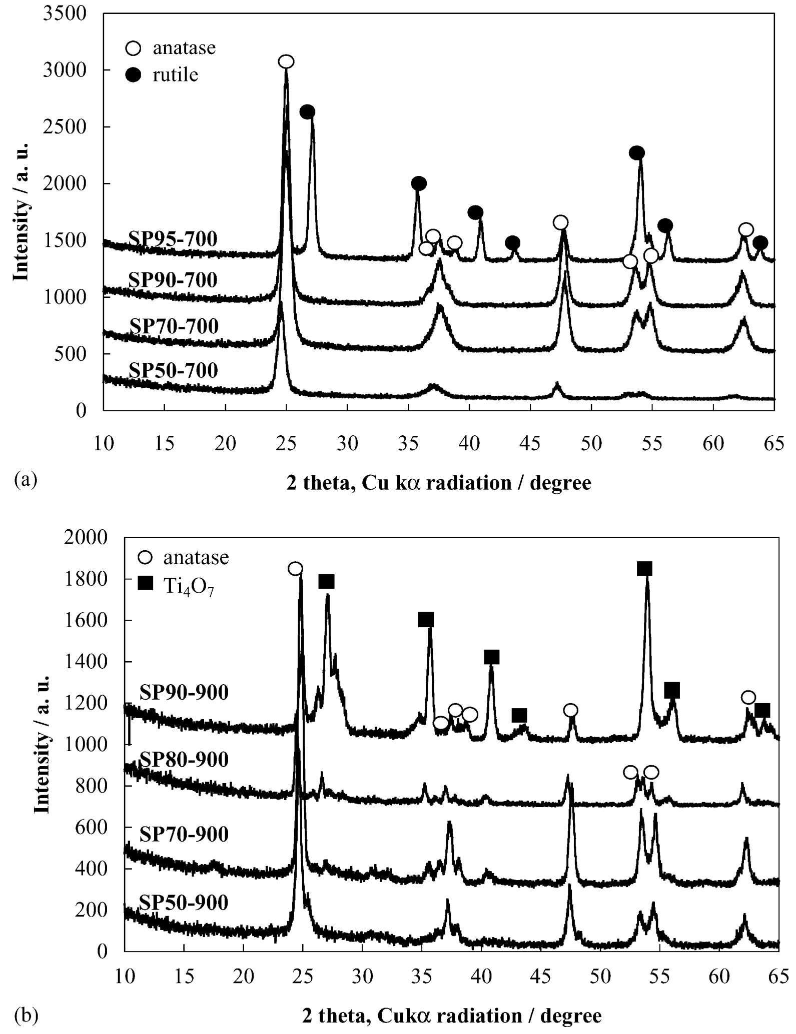


Fig. 3. XRD patterns of samples: (a) heated at 700 °C and (b) heated at 900 °C.

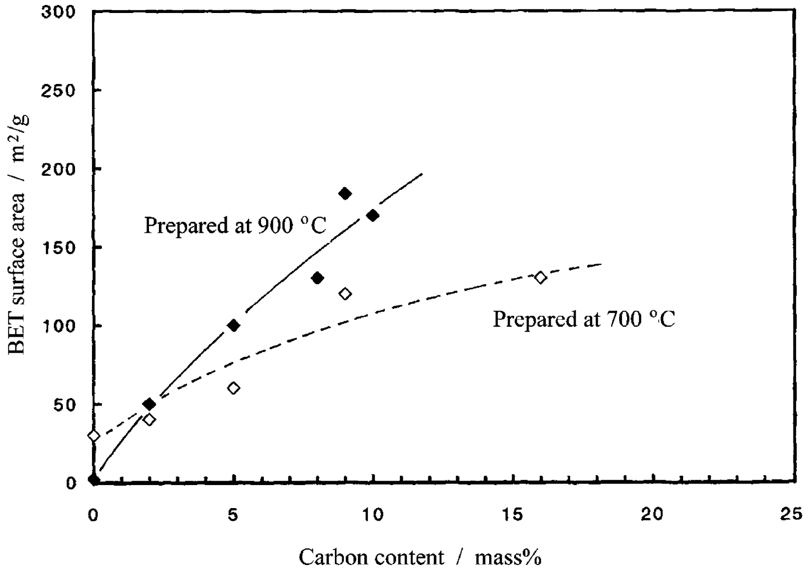


Fig. 4. Change in BET surface area with carbon content in carbon-coated anatase samples.

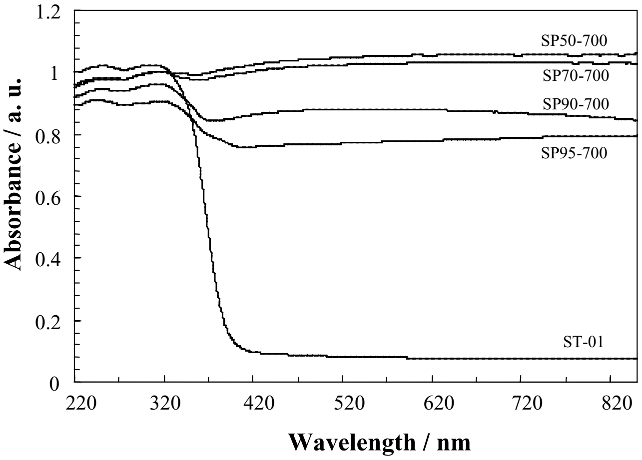


Fig. 5. Optical absorption spectra of samples.

and also the absorption edge due to anatase becomes more ambiguous, but still the absorption edge can be seen from the enlarged spectra.

It is worthwhile to point out that a trace of absorption edge due to anatase is detected even in the SP50-700 sample of high content of carbon (about 15 mass%). These results proved that UV rays coming through the carbon layer could irradiate anatase surface and excite the semiconductor, though their intensity might be weakened.

3.3. Adsorption of methylene blue and Reactive Black 5

In Fig. 6 the relative concentration of MB remained in the solution in the dark (the adsorption of MB) was shown for the samples of different carbon content heated at 700 °C, 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. However, carbon-coated samples show marked adsorption of MB. Samples SP50-700 and SP70-700, which have high carbon contents, adsorb whole MB in the solution within 10 min. The changes of relative concentration of MB solution during adsorption on SP90-700 and SP95-700 seem to occur in two steps, very quick adsorption at the beginning and then slow one. In the first step MB concentration decreases to about 3 and 26% for SP90-700 and SP95-700, respectively, and then complete adsorption takes about 15 and 25 h, respectively.

These results clearly show two types of MB adsorption on carbon-coated TiO_2 particles: rapid and slow one. The former is supposed to be due to the adsorption of MB into micropores of coated carbon layer with a high BET surface area (Table 1), similar to that on activated carbon. The latter is observed for ST-01 and ST-01-700 samples. MB adsorbed slowly onto aggregated particles of TiO_2, which was probably caused through the MB condensation on the particles surface, because TiO_2 particles looked blue at the end of adsorption. From the results shown in Fig. 6, decreasing rate of the relative MB concentration is much faster for the carbon-coated TiO_2 samples than for ST-01, because of the predominant adsorption, not condensation.

Reactive Black 5 also adsorbed quickly in high quantity on the carbon-coated catalysts, whereas ST-01 showed very small adsorption. In general, adsorption capacity of Reactive Black 5 on carbon-coated catalysts was proportional to their BET surface area, but higher adsorption was observed on catalysts heated at 900 °C. In Fig. 7 measured adsorption capacity of MB and RB5 on carbon-coated catalysts is presented versus BET surface area of catalysts. MB adsorbed in higher quantity on the catalysts heated at 700 °C than that heated at 900 °C in the range of the same BET surface area of catalysts, but the highest MB adsorption was observed on the sample heated at 900 °C, having the highest value of BET.

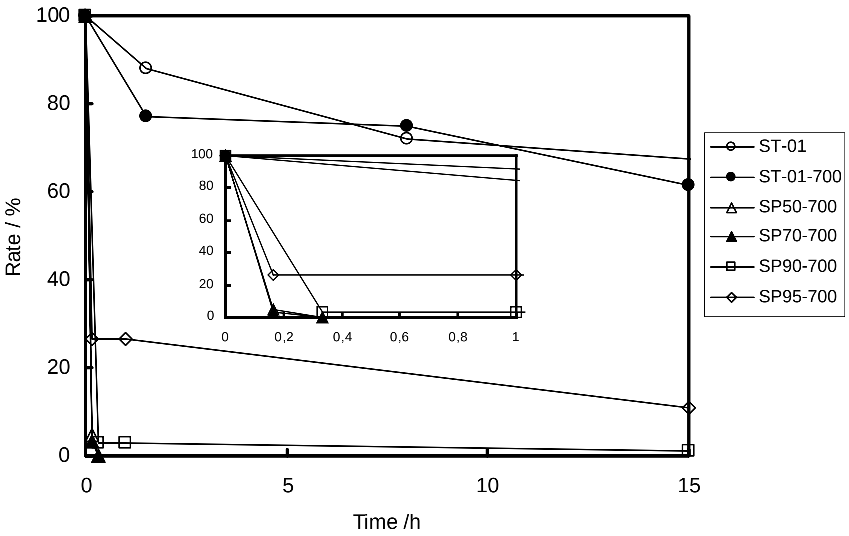


Fig. 6. Changes in relative concentration of methylene blue in the dark with time due to absorption by samples.

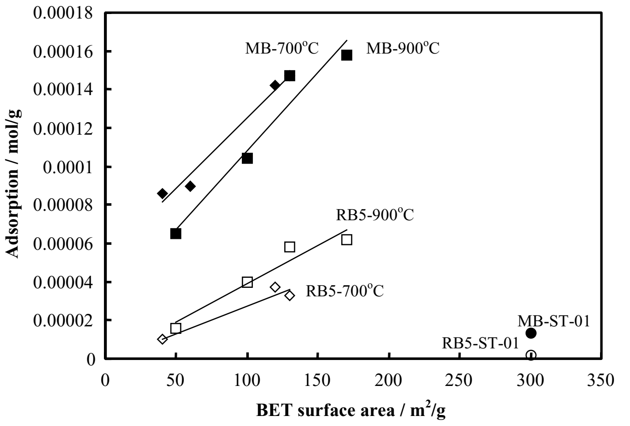


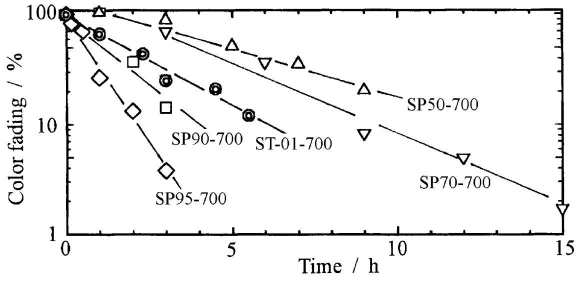
Fig. 7. Adsorption capacity of MB and RB5 on ST-01 and carbon-coated TiO_2 catalysts.

Original ST-01 showed almost no adsorption of RB5. Generally adsorption of MB molecules on the catalysts was higher than RB5 what can be explained by the difference in the molecules size of MB and RB5. The molar weight of MB is 392 g/mol, whereas Reactive Black 5 is more than two times larger, having molar weight of 992 g/mol.

3.4. Photodecomposition of methylene blue and Reactive Black 5

Changes of MB concentration with time of UV irradiation on ST-01-700 and carbon-coated TiO_2 samples are shown in Fig. 8, where relative concentration of MB is plotted in the logarithmic scale. Photodecomposition of MB on ST-01 was the same as on ST-01-700.

a) Carbonized at 700 °C



b) Carbonized at 900 °C

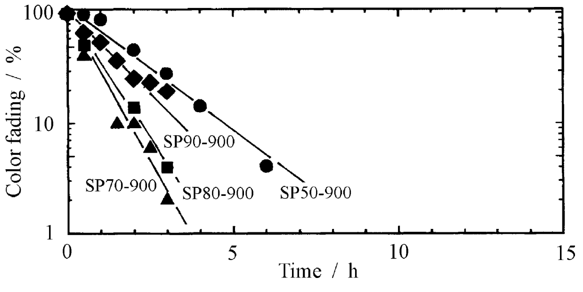
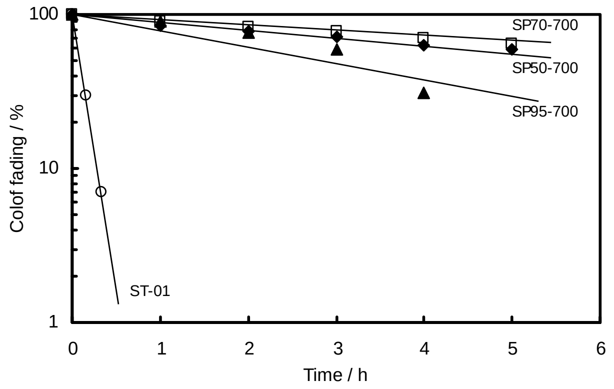


Fig. 8. Changes in relative concentration of MB in the solution with UV irradiation time.

a) ST-01 and carbon-coated TiO_2 carbonized at 700°C



b) carbon-coated TiO_2 carbonized at 900°C

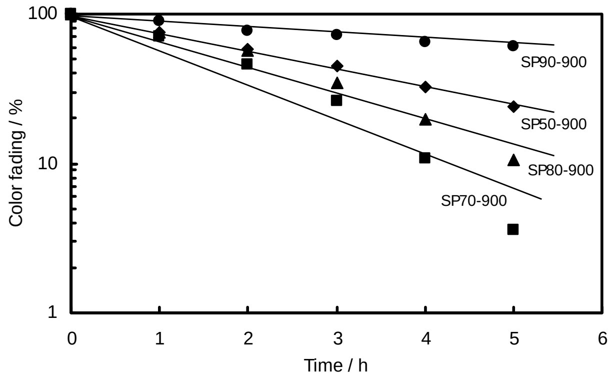


Fig. 9. Changes in relative concentration of RB5 in the solution with UV irradiation time.

In Fig. 9 the changes of relative concentration of RB5 solution are plotted versus the time of UV irradiation. It's worth to note, that ST-01 decolorized RB5 solution completely within 1 h.

Rate constant k of photodecomposition of both, MB and RB5 can be calculated from the linear slope of the relation between $\ln(c/c_0)$ and kt, where c_0 and c are the concentration of starting solution and that after UV irradiation in time t (h), respectively. The values of rate constant k of MB and RB5 photodecomposition are presented in Table 1.

In comparison with the original ST-01, most of carbon-coated TiO_2 samples can decompose MB with much higher rate. Slow decomposition of MB on SP50-700 and SP70-700 is reasonably supposed to be due to the thick layer of coated carbon. In Fig. 10, rate constant k for MB and RB5 decomposition under UV irradiation is plotted against carbon content in carbon-coated TiO_2 catalysts.

Fig. 10 shows that there is not unique relation between rate constant k and the content of carbon, however both, MB and RB5 showed the same dependence. Most of carbon-coated samples have much higher k value than original ST-01 for MB decomposition, but for RB5 decomposition it's opposite. It means, that mechanism of MB and RB5 decompositions is quite different. MB decomposes on TiO_2 through the adsorption on the catalyst surface. For

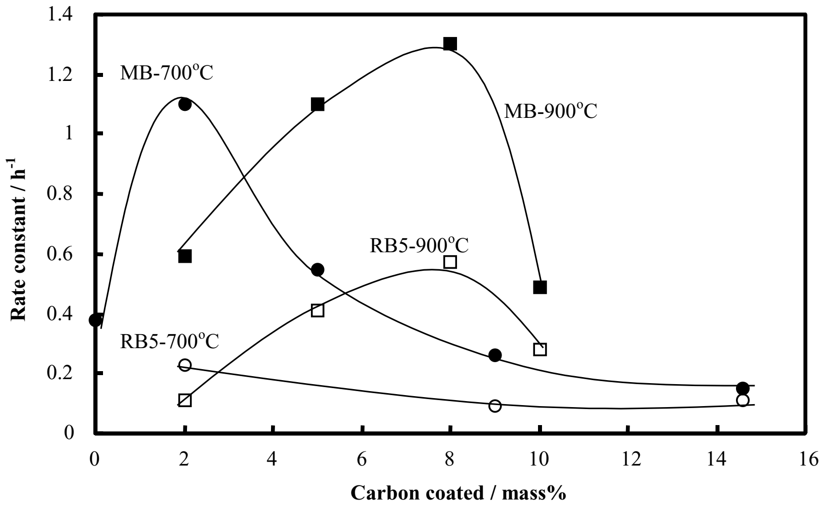


Fig. 10. The rate constant changes for methylene blue photodecomposition in relation to the content of carbon in carbon-coated anatase samples.

this reason almost all carbon-coated TiO_2 catalysts showed higher rate of MB decomposition than ST-01. RB5 is poorly adsorbed on the surface of TiO_2, so RB5 decomposition does not depend on the adsorption on the catalyst surface. ST-01 showed higher decomposition rate in this case than carbon-coated TiO_2 catalysts. The fact, that the same carbon-coated TiO_2 catalysts had the highest rate constants for both, MB and RB5 means that the same parameters of catalyst, such as crystalline structure, phase composition, and thickness of carbon layer govern the process of photodecomposition.

In our previous paper on anatase without any carbon coating [23], crystallinity of anatase was pointed out to be important factor influenced on the rate of photodecomposition, where half width of 1 0 1 X-ray diffraction line of anatase phase was used as a measure of crystallinity. Therefore, on the present carbon-coated samples, rate constant k is shown as a function of a half width of 1 0 1 line (Fig. 11).

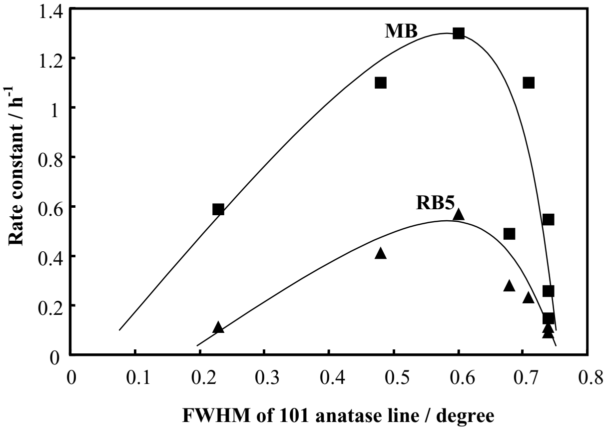


Fig. 11. Dependence of rate constant k for MB and RB5 photodecomposition on the half width of 1 0 1 diffraction line of anatase phase.

From Fig. 11 it is observed, that there is no clear relation between half width of anatase 1 0 1 peak and rate constant k, the higher constant rate was noted for the carbon-coated sample consisted with a single anatase phase and the sharpest anatase peak in comparison with the other samples of a single anatase phase. Although the anatase 1 0 1 peak became sharper in the other carbon-coated samples, anatase coexisted with the rutile or reduced Ti_4O_7 phase of lower photocatalytic activity.

4. Concluding remarks

ST-01 heated at 700 °C showed sintering of TiO_2 particles. At the same time the growth of crystals occurred and anatase transformed to rutile what finally resulted in high reduction of BET surface area of ST-01. In carbon-coated TiO_2 samples heated at 700 °C, not only sintering of aggregated particles but also crystal growth in each particles were depressed, what influenced on the suppression of the phase transformation from anatase to rutile at high temperatures of heat treatment.

It was experimentally shown that high crystallinity of anatase phase in carbon-coated TiO_2 samples was important factor accelerating the photodecomposition of MB [23]. Partial transformation of anatase to rutile in TiO_2 catalysts reduced their photocatalytic activity.

Presented results showed that color fading of MB solution was due to the adsorption and decomposition of MB, and adsorbed MB into carbon layer was decomposed by UV irradiation on TiO_2 particles. The suppression of the phase transformation from anatase to rutile by carbon gives certain advantages for the carbon-coated TiO_2 catalysts, conducting finally to increase the catalysts activity. But at the same time this effect of improvement catalyst activity was not observed for RB5 decomposition. It means, that prepared carbon-coated catalysts have selective application. It can be interested to develop their application for the other organic compounds.

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References

[1] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Hermann, Appl. Catal. B: Environ. 39 (2002) 75.
[2] J. Grzechulska, A.W. Morawski, Appl. Catal. B: Environ. 36 (2002) 45.
[3] B. Zieliñska, J. Grzechulska, B. Grzmil, A.W. Morawski, Appl. Catal. B: Environ. 35 (2001) L1.
[4] T. Sauer, G. Cesconeto Neto, H.J. José, R.F.P.M. Moreira, J. Photochem. Photobiol. A: Gen. 149 (2002) 147.
[5] I. Ilisz, A. Dombi, K. Mogyoróshi, A. Farkas, I. Dékány, Appl. Catal. B: Environ. 39 (2002) 247.
[6] D.S. Muggli, L. Ding, Appl. Catal. B: Environ. 32 (2001) 181.
[7] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B: Environ. 42 (2003) 319.
[8] A.D. Modestov, O. Lev, J. Photochem. Photobiol. A: Chem. 112 (1998) 261–270.
[9] Y. Suwa, M. Inagaki, S.J. Naka, Mater. Sci. 19 (1984) 1397.
[10] I. Izumi, K. Kuroda, Y. Ohnishi, T. Tsumura, N. Iwashita, Mizusyori Gizyutu 42 (2001) 461 (in Japanese).
[11] T. Tsumura, N. Kojitani, I. Izumi, N. Iwashita, M. Toyoda, M. Inagaki, J. Mater. Chem. 12 (2002) 1391.
[12] T. Tsumura, N. Kojitani, H. Umemura, M. Toyoda, M. Inagaki, Appl. Surf. Sci. 196 (2002) 429.
[13] M. Toyoda, T. Tsumura, Y. Nanbu, M. Omura, M. Inagaki, Mizukannkyou Gakkaishi 26 (2003) 209 (in Japanese).
[14] M. Inagaki, H. Miura, H. Konno, J. Eur. Ceram. Soc. 18 (1998) 1011.
[15] M. Inagaki, Y. Okada, V. Vignal, H. Konno, K. Oshida, Carbon 36 (1998) 1706.
[16] M. Inagaki, Y. Okada, H. Miura, H. Konno, Carbon 37 (1999) 329.
[17] M. Inagaki, K. Fujita, Y. Takeuchi, K. Oshida, H. Iwata, H. Konno, Carbon 39 (2001) 921.
[18] H. Konno, H. Miura, K. Oyamada, M. Inagaki, ATB Metall. 37 (1997) 149.
[19] H. Konno, K. Oyamada, M. Inagaki, J. Eur. Ceram. Soc. 20 (2000) 1391.
[20] T. Tsumura, A. Katanosaka, I. Souma, T. Ono, Y. Aihara, J. Kuratomi, M. Inagaki, Solid State Ionics 135 (2000) 209.
[21] M. Inagaki, Y. Hirose, S. Takeuchi, Res. Rep. Aichi Inst. Tech. 4 (2002) 7 (in Japanese).
[22] M. Inagaki, Y. Hirose, T. Matsunaga, T. Tsumura, M. Toyoda, Carbon 41 (2003) 2619.
[23] M. Toyoda, Y. Nanbu, Y. Nakazawa, M. Hirano, M. Inagaki, Appl. Catal. B: Environ. 49 (2004) 227.