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Comparison of physical properties and dye photo-degradation effects for carbon/TiO_2 complexes

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Abstract We have studied a method for the preparation of hybrid carbon/TiO_2 complexes involving pitch coating, pitch binding and the penetration of titanium n-butoxide (TNB) solution with porous carbon. The photocatalysts were investigated with surface textural properties and SEM morphology, structural crystallinity and elemental identification between porous carbon and TiO_2, and dye decomposition performance. For the all carbon/TiO_2 complexes prepared by some kinds of different methods, the excellent photocatalytic effect for dye degradation should be attributed to the both effects between photo-decomposition of the supported TiO_2 and adsorptivity of the porous carbons.

Key words Porous carbon, Surface area, SEM, XRD, EDX, Photocatalyst

1. Introduction

More recently, numerous studies have shown their unique performance in photo degradation of chemical toxic components in wastes, such as phenols and aromatic compounds. The combination of carbonaceous materials with photocatalysts has been of interest. We also have been interested in the carbon-titania technologies, and have found through our investigation that it is important to quantify the impact that irradiations of the carbon/TiO_2 have a photocatalytic activity. The roles of carbon at the carbon/anatase-type titanium dioxide complex were found to give many advantages such as high photosensitivity, high photocatalytic activity and high adsorptivity [1-3]. A number of studies have shown their unique performance in photodegradation of most organic toxic compounds in wastewater [4, 5]. According to former studies for the carbon sources, the carbonization of an unlinked resorcinol resin with titanium tetrabutoxide [6], immersion of activated carbon in a TiO_2 sol [7], and mechanical grinding of activated carbon with TiO_2 [8] have been reported for the preparation of carbon/TiO_2 composites. According to early study [9], it suggested that the contaminant molecules in carbon-coated TiO_2 have to be adsorbed into the carbon layer that covers the TiO_2 particle, diffuse through the carbon layer to reach the surface of the TiO_2 photocatalyst and then be decomposed under UV irradiation. We also have been interested in the carbon/titania complexes studies and their technologies, and have found through our investigation that it is important to quantify the impact that the carbon/TiO_2 complex particles give adsorption ability to the catalyst particles, to transfer the adsorbates to the surface of the TiO_2. Composite product of carbon and TiO_2 photocatalysts may be offers the merits like an adsorption effect on the porous structure and light excitation source for the photocatalytic degradation for the pollutants. Among the various supports, porous carbon give very promising for the some kinds of reasons; adsorption and release capability for the pollutants onto the surface of TiO_2, increasing of charge transference between porous carbon and TiO_2 by acidification of surface hydroxyl groups and adsorption of intermediates produced during degradation.

In this study, we have prepared to hybrid composite of carbon and titanium oxide with synergistic effects by the combined function of adsorptivity and photoactivity. The preparation methods of hybrid carbon/TiO_2 complexes were used for pitch coating, pitch binding and the penetration of titanium n-butoxide (TNB) solution with porous carbon. The studied catalysts were characterized by BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX) and UV/VIS spectrophotometer. The catalytic efficiency of the developed catalysts was evaluated by the photodegradation of methylene blue (MB).

2. Experimental

2.1. Materials

A granular type activated carbon used in this study

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was prepared from coconut shell. The coconut shell was carbonized first at 773 K, and then activated by steam diluted with nitrogen in a cylinder quartz tube at the temperature range of 1023 K for 30 min. These activated carbons were washed with deionized water and dried overnight at ambient temperature. Self-made ACFs used as a raw material were prepared from commercial PAN fibers (T-300 Amoco, USA). The carbonized PAN fiber was heated first at 823 K for burn off, and the carbon fibers were activated by steam diluted with nitrogen in a cylinder quartz glass tube in the temperature of 1073 K for 30 min. The 0.5 M diluted nitric acid at boiling temperature was used in the oxidation treatment to increase the formation of functional groups without the damage of the ACF surface. The oxidation was carried out at the boiling temperature for 1 hour. The oxidized ACFs were washed and dried at 323 K for 24 hours. The pitch was used carbon precursor and binder material for preparation of carbon/TiO_2 complexes photocatalysts. The granular pitch was supplied from Jungwoo Chemical Co. (Korea). The TiO_2 photocatalysts was commercially available (Duk-San Pure Chemical Co., Korea), which was composed of a single phase of anatase with secondary particles of about 80~150 μm aggregated from the primary particles of about 30~50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area about 125 m^2/g. For the melting of pitch, carbon tetrachloride (Dae-Jung Chemical Co., Korea) was used as solvent. After melting of pitch as coating and binder material in CCl_4 solution, TiO_2 powder and carbon sources were mixed with pitch-CCl_4 solution. The powder mixtures in the solution before the preparation of carbon/TiO_2 complexes were heated at 333 K for 6 hours. After heating, the solvent in the mixtures was vaporized at 353 K for 1 hour. We prepared activated carbon fiber slurry solutions with pristine concentrations of 20 ml of titanium n-butoxide (TNB, $C_{16}H_{36}O_4Ti$, Acros Organics, USA) for the preparation of ACIDAFT55 complexes. For the preparation, 5 g of powdered activated carbon were mixed in to 20 ml of TNB aqueous solutions and stirred for 5 hours at 333 K. The agglomerates of carbon/TiO_2 complexes prepared was heated at 973 K for 1 hour and then crushed at auto miller. The nomenclatures and preparation conditions of samples were listed in Table 1.

2.2. Characterization

For the physical parameter measurements, nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics, U.S.A) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of carbon/TiO_2 complexes prepared through the CCl_4 dissolution and TNB method. For the elemental analysis in carbon/TiO_2 complexes, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimadzu XD-D1, Japan) with Cu Kα radiation. As one of the analysis of photocatalytic activity, UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize of catalytic efficiency of carbon/TiO_2 complex photocatalysts. Characterization of methylene blue ($C_{16}H_{18}N_3S$, MB) in water was determined by the following procedure. A carbon/TiO_2 complexes powdered sample of 0.05 g was dispersed in an aqueous solution with a concentration of 5.0×10^{-5} mol/l in the dark atmosphere at room temperature. Each concentration was measured as a function of UV irradiation time from the absorbance at the range of 550~750 nm wavelength of MB measured by UV/VIS spectrophotometer.

2.3. Photocatalytic effect

In order to reveal the photocatalytic effect of the carbon/TiO_2 complexes prepared, the decomposition reaction of MB in water was followed. Powdered samples of 0.05 g were dispersed in ultra sonicate for 3 min. For UV irradiation the UV lamp (20 W, 365 nm) was used at the distance of 100 mm from the solution in darkness box. By sampling 3 ml of solution after removal of dispersed powders through centrifuge, the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

Table 1
Nomenclatures of samples prepared as different types of carbon forms to titanium sources

Sample	Mixing ratios (wt%)	Nomenclatures
Pitch + TiO_2	30 : 70	PT30
Pitch + Activated Carbon + TiO_2	20 : 40 : 40	PAT244
Pitch + Activated Carbon Fiber + TiO_2	20 : 40 : 40	PAFT244
Acid treated Activated Carbon Fiber + TNB	(0.5 M HNO_3)ACF 3 g + TNB 30 ml	ACIDAFT55

3. Results and Discussion

3.1. Surface properties and morphology

The surface characteristics of the carbon/TiO_2 complexes prepared from mechanical methods are compiled in Table 2. By using ceramic substrate, carbon coating was experimentally exposed that the carbon formed on most ceramic surface from carbon precursors was very microporous [9]. The BET surface area for pitch-coated TiO_2 (PT30) prepared at 873 K give a low value with common dependence on pitch content. It is plausible assume that thin carbon layers derived from pitch on TiO_2 particles are responsible for the BET surface area. According to the former study [10], it was found that the original pristine TiO_2 give very small surface area (about 2 m^2/g). In our case, it was obtained that the BET surface area for the carbon layer in the sample increases to increasing with pitch contents. The result of the table for the PAT244 demonstrates that the sample is a slight increase in the BET surface area as complex samples by addition of activated carbon. However, almost all surface textural parameters for the complex are a considerably more decrease than that of pristine activated carbon. This can be attributed to the blocking of micropores during pitch coating. It is expected that the dissolved pitch can be blocked to pore in activated carbon, but porosity of carbons is reproduced by heat treatment. It is noteworthy that increases of surface parameters among composite series are related to removal efficiency of dye and other pollutants by adsorptivity. The TiO_2 only presented some macropore and did not present either mesopore or micropore. Consequently, they had low surface area value. The optimum mixing ratio was 20 : 40 : 40 between activated carbon and TiO_2. The result of the table for the PAFT244 demonstrates that the sample is a slight more increase in the BET surface area with an addition of activated carbon fiber than that of PAT244. However, almost all surface textural parameters for the samples are a considerably more decrease than that of pristine activated carbon fiber. From the Table 2, it can be seen that both the BET surface area and the total pore volume decrease as the distribution of TiO_2 on the activated carbon fiber surfaces after acid treatments. Oh *et al.* [11, 12] reported that the BET surface area is considerably decreased due to the blocking of the narrow pores by surface complexes introduced by pre-treated acids. Almost all surface textural parameters for the complexes are a considerably more decrease than that of pristine activated carbon fiber. This can be attributed to the blocking of micropores of titanium complexes by surface modification of activated carbon fiber treated with nitric acid. It is expected that the formation of titanium complexes with increasing of the surface functional groups can be blocked to pore in the activated carbon fiber surfaces, but porosity of carbons is reproduced by heat treatment.

The surface structures of the carbon/TiO_2 complexes were investigated and the relationship among binder pitch deposition, porous carbon and pristine TiO_2, and change of their structure were investigated. Figure 1 shows SEM micrographs of various carbon/TiO_2 complexes as a function of using some kinds of carbons. The figure presents the results from the characterization of porous texture on the carbon/TiO_2 complexes and pitch or carbon and TiO_2 mechanical distributions on the surfaces for all the materials used. In case of Fig. 1(a), when carbon derived from pitch is dispersed onto TiO_2, the surface properties are modified in some cases, this effect being developed as microporosity in PT30 with porosity. SEM pictures of PT30 provide information about the distribution of carbon on the TiO_2 surface. In case of Fig. 1(b), it was observed that pitch was covered with activated carbon/TiO_2 particles. The TiO_2 particles regularly distributed on the around of activated carbon with carbon precursor pitch. And some large

Table 2
Surface textural properties of pristine materials and samples prepared as different types of carbon/TiO_2 complexes

Samples	Parameter			
	S_{BET} (m^2/g)	Micropore volume (cm^3/g)	Internal Surface Area (m^2/g)	Average Pore Diameter (Å)
As-received TiO_2	125.0	-	87	-
As-received Activated Carbon	1829	0.412	1597	17.28
As-received Activated Carbon Fiber	1989	0.443	1645	17.56
PT30	348	0.213	264	12.33
PAT244	762	0.312	636	14.83
PAFT244	881	0.315	679	15.01
ACIDAFT55	976	0.326	772	16.12

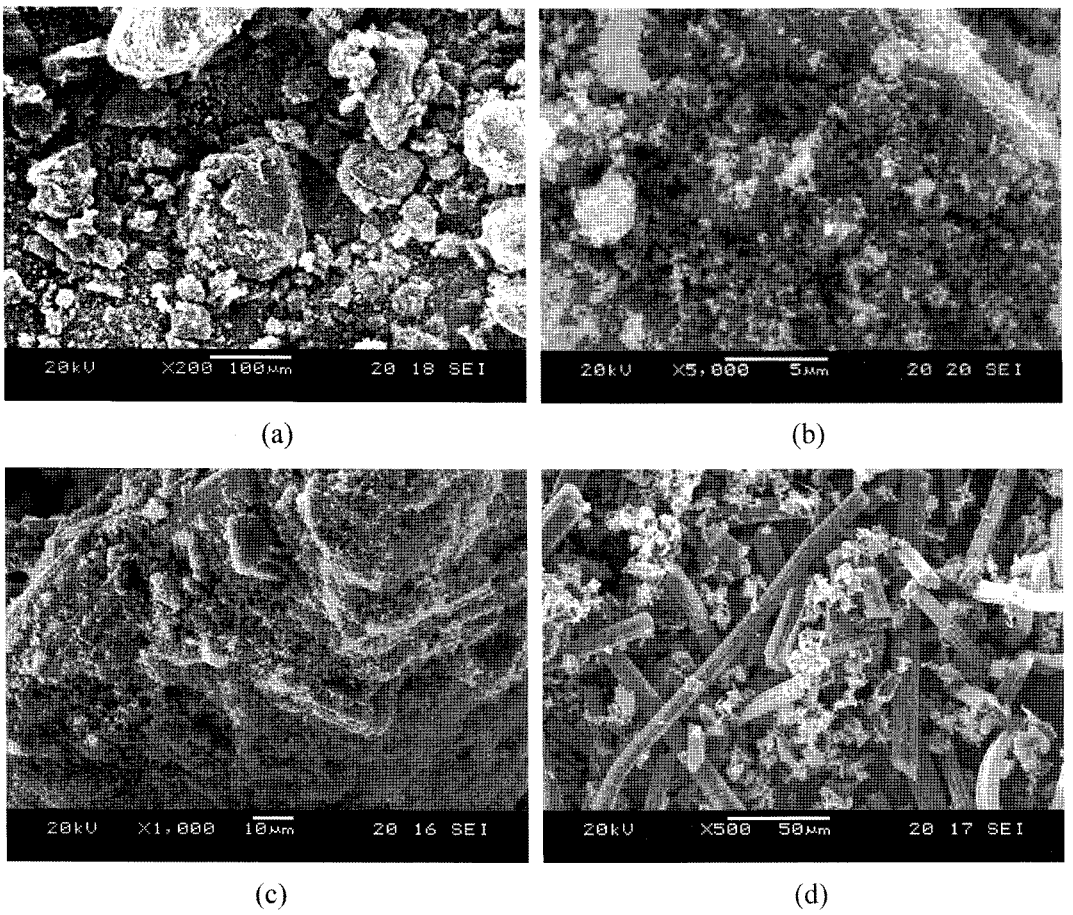

Fig. 1. SEM micrographs of carbon/TiO_2 complexes; (a) PT30, (b) PAT244, (c) PAFT244 and (d) ACIDAFT55.

clusters were found from the activated carbon surfaces. In contrast, homogenous activated carbon and TiO_2 distribution with good particle dispersion was observed when the mixing ratio was 20 : 40 : 40 between activated carbon and TiO_2. It was considered that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. It was reported [13] that the quantum efficiency of the electron from the photocatalyst particle interior to the surface and the recombination rate of electron-hole pairs of the photocatalyst. From the result of Fig. 1(c), it was observed that pitch was covered with ACF/TiO_2 particles. The TiO_2 particles irregularly mounted on the around of ACF with carbon precursor pitch. In this study, the samples obtained after heating with pitch and TiO_2 with various mixing ratio of activated carbon fiber were shown granular and stick-like form above 1023 K. The carbon coated solid particles has been reported on the various typed titania [14, 15]. The activated carbon fiber and TiO_2 particles become pronounced and coarse by pitch treatment and the size of the particles is kept large. The aggregated secondary particles with a diameter size of around 10~20 μm are observed. Most of the particles and stick-like forms are sintered with each other, becoming aggregated though a small amount of small particles still remain. According to Fig. 1(d), the titanium complexes particles derived from TNB solution on the carbon fiber surfaces become pronounced

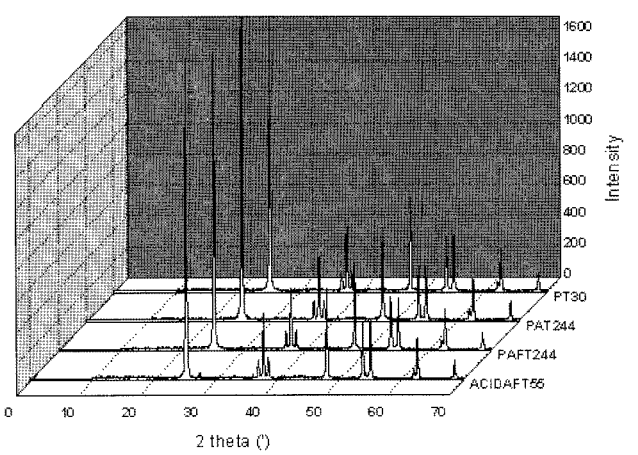

Fig. 2. XRD patterns of the carbon/TiO_2 complexes heat-treated at 903 K.

and coarse by acid treatment and the size of the particles is kept large with acid treatment effect.

3.2. Structural and elemental identifications

In Fig. 2, changes in XRD pattern are shown on the carbon/TiO_2 complexes prepared with some kinds of preparation methods. The TiO_2 structure was shown typical anatase type. The major peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the developed TiO_2 existed in anatase state. But, a weak and broad carbon peak of graphene peaks were not observed in the X-ray diffraction patterns for the carbon/TiO_2 complexes due to very weak peak intensity compare to that of anatase. The XRD patterns of all of

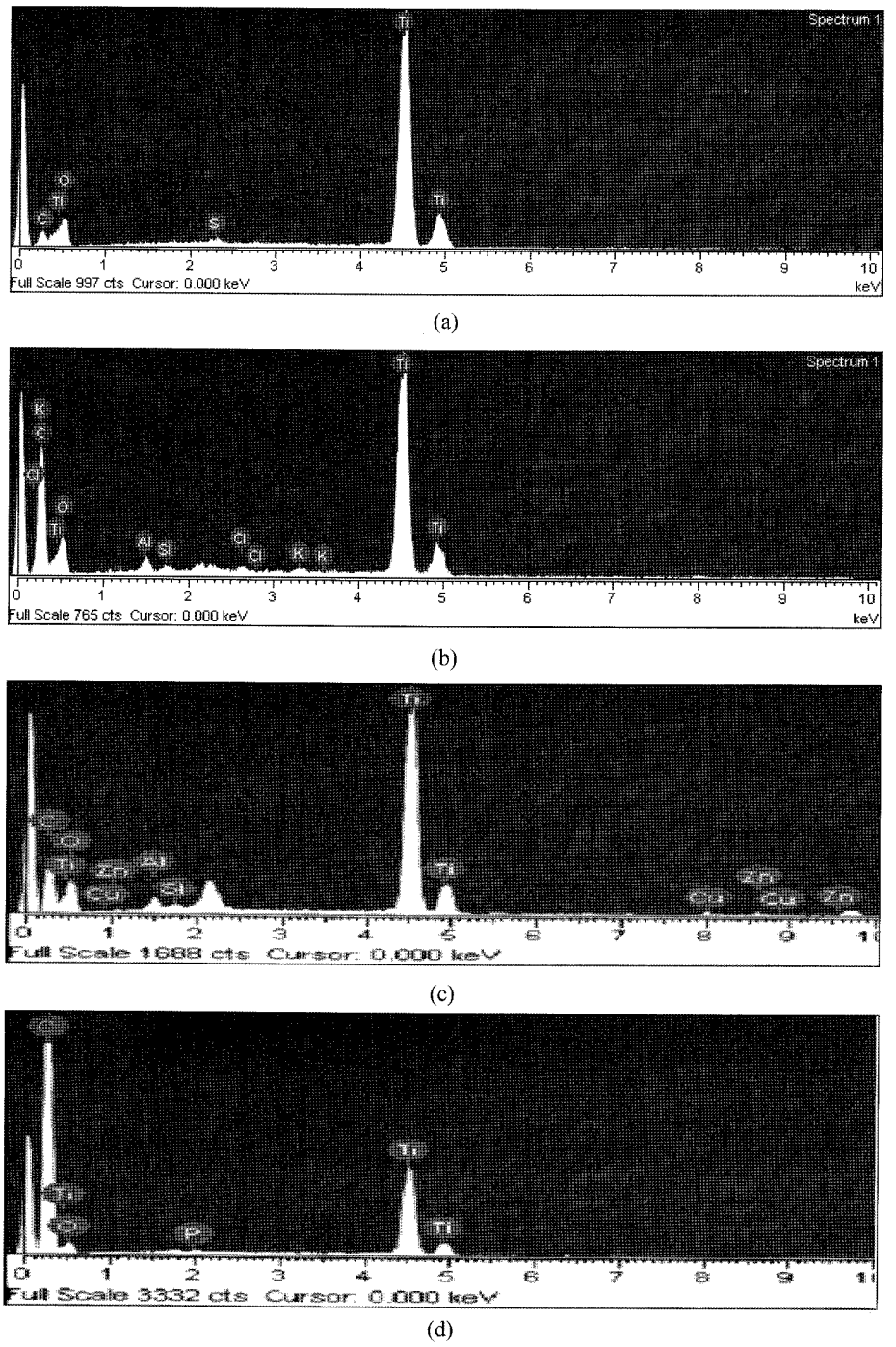

Fig. 3. EDX elemental microanalysis of carbon/TiO_2 complexes prepared by some kinds of methods; (a) PT30, (b) PAT244, (c) PAFT244 and (d) ACIDAFT55.

Table 3
EDX Elemental Microanalysis of carbon/TiO_2 complexes prepared as different types

Sample	C	O	Ti	Others
PT30	8.00	36.4	55.2	0.39
PAT244	38.6	27.6	31.9	1.90
PAFT244	68.8	12.9	18.2	0.10
ACIDAFT55	21.5	26.5	51.9	0.10

the carbon/TiO_2 complexes showed the formation of anatase crystallites. In case of ACIDAFT55, this indicates that was well dispersed inside and outside ACF matrix, with the formation of a crystal. After the heat treatment at 973 K for 1 hour, the main crystalline phase was presented to anatase structure by transformation of TNB.

For the elemental microanalysis of carbon/TiO_2 complexes as a function of some kinds of preparation methods, these samples were analyzed by EDX. The EDX spectra of carbon/TiO_2 complexes were shown in Fig. 3. Most of these samples are richer in carbon and major Ti metal than any other elements. These spectra show the presence of C and O with strong Ti peaks and some kinds of metallic peaks as impurity. The results of EDX elemental microanalysis of carbon/TiO_2 complexes were listed in Table 3. In the case of most of the samples, carbon and Ti were present as major elements in the carbon/TiO_2 complexes. These results were observed for each sample show the spectra corresponding to almost all complexes rich in C atom as major element.

3.3. Dye decomposition by photocatalytic activity

The results of dye decomposition could be obtained by UV/VIS spectroscopy. The UV/VIS absorbance spectra of MB initial concentration at 5.0×10^{-5} mol/l against the carbon/TiO_2 complexes prepared by some kinds of preparation methods are shown in Fig. 4. The values of absorbance maxima for the all samples slowly decrease with increase of UV irradiation time. This indicates that the transparent of the MB concentration highly increase by photocatalytic degradation effect of

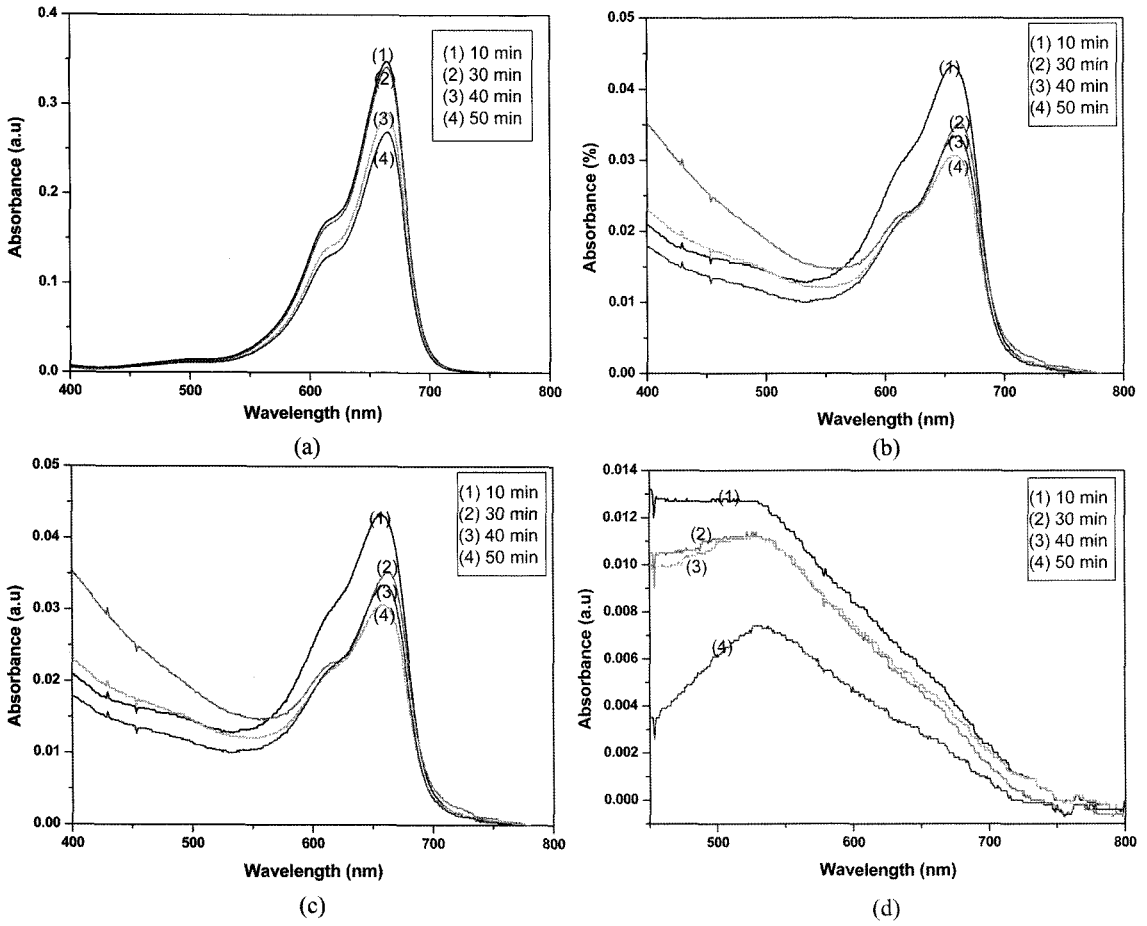

Fig. 4. UV/VIS spectra of absorbance variation against the carbon/TiO_2 complexes under various time conditions; (a) PT30, (b) PAT244, (c) PAFT244 and (d) ACIDAFT55.

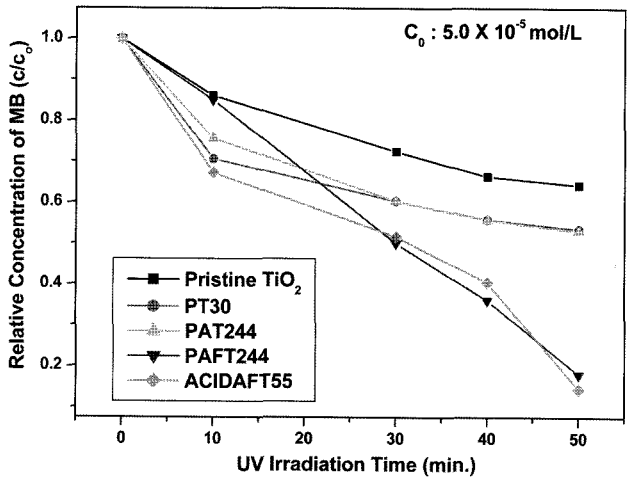

Fig. 5. Dependence of dye decomposition in the aqueous solution on time of UV irradiation for the carbon/TiO_2 complexes.

carbon/TiO_2 complexes. Figure 5 presents changes in MB concentration under UV light irradiation in the solution after dispersion of carbon/TiO_2 photocatalysts. The dye removal with carbon/TiO_2 photocatalysts is carried out to observe the photo-degradation effect for the MB solution. It is observed that the dye in the solution is quite unstable with variation of concentration when it is irradiated under photo with carbon/TiO_2 photocatalysts, suggesting that the disappearance of dye caused by UV irradiation is presented. The changes are plotted on the relative concentration (c/c_0) of MB in the aqueous solution with UV irradiation time for the carbon/TiO_2 complexes. The approximately linearity was shown the plot depending on irradiation time, as reported on similar modified TiO_2 samples [16, 17]. Because the porous carbon in carbon/TiO_2 complexes had a large adsorptivity, it is believed that the decrease of dye concentration in the aqueous solution can be occurred in two physical phenomena such as adsorption by porous carbon and photo-decomposition by TiO_2 formed on the carbon surfaces. By the former study [18-20], MB adsorbed on the carbon particles can be eventually decomposed by the TiO_2 particles in solution. These suggest that the TiO_2 formed on the surface of activated carbon can retain its photocatalytic reactivity. The two physical effects have been ascribed [19, 20] the enhanced adsorption of the pollutants on activated carbon followed by a transfer through an interphase to titania. The photocatalytic activity in the carbon/TiO_2 complexes could be attributed to the homogeneous distribution between titania complexes and porosity on the external surface. In case of ACIDAFT55, the surface oxidation of activated carbon fiber by acid treatment can be occurred the acid-base character of the surface active sites of the oxides. The surface acidic functional groups of the active sites of the oxides can be determined by means of indirect determination, such as measurements of the catalytic activity for the decomposition of pollutants [6]. From the dye removal results measured periodically over 60 min, the increase in the porosity like surface area results in a significant degradation effect with decrease of c/c_0 of MB solution. For the all carbon/TiO_2 complexes prepared by some kinds of different methods, slope relationship between c/c_0 of MB and UV irradiation time were observed at 5.0×10^{-5} mol/l of MB concentration. From the results between c/c_0 of MB and UV irradiation time, it was observed that dye removal efficiency in the composites is better excellent then that of pristine TiO_2. We therefore can conclude that the effect of dye degradation should be attributed to the both effects between photo-decomposition of the supported TiO_2 and adsorptivity of the porous carbons.

4. Conclusion

In this study, we have prepared carbon/TiO_2 complexes photocatalysts with some kinds of modified methods. The photocatalysts were investigated with surface textural properties and SEM morphology, structural crystallinity and elemental identification between porous carbon and TiO_2, and dye decomposition performance. The result of the textural surface properties presents that the increase in the porosity like surface area results in a significant degradation effect. The SEM morphologies present to the surface structure on the carbon/TiO_2 complexes. In the XRD patterns for all carbon/TiO_2 complexes, the diffraction peaks are shown the formation of anatase crystallites. The EDX spectra show the presence of C, O and Ti peaks with rich carbon and Ti element. Finally, the photocatalytic activity of the carbon/TiO_2 complexes between c/c_0 for MB and UV irradiation time could be attributed to the both effects between photocatalysis of the supported TiO_2 and adsorptivity of porous carbon.

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