

Characterization of AC/TiO₂ Composite Prepared with Pitch Binder and Their Photocatalytic Activity

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Received July 10, 2006

In this study, we have prepared pitch binded AC (activated carbon)/TiO₂ composites photocatalysts through carbon tetrachloride solvent method. The developed samples were characterized with surface properties, structural crystallinity between AC and TiO₂, elemental identification and photocatalytic activity. The results of the textural surface properties demonstrate that there are slight increases in the BET surface area and adsorbed volume from adsorption isotherm of composite samples with increasing of the amount of AC. The SEM results present to the characterization of porous texture on the pitch/AC/TiO₂ composites and homogenous compositions in the particle for all the materials used. From XRD data, a weak and broad carbon peak of graphene remained rutile peaks kept with anatase structure were observed in the X-ray diffraction patterns for the pitch/AC/TiO₂ composites. The EDX spectra show the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and major Ti metal than any other elements. Finally, the excellent photocatalytic activity of the pitch/AC/TiO₂ composites between relative concentration (*c/c*₀) of MB and UV irradiation time could be attributed to the both effects between photocatalysis of the supported TiO₂ and adsorptivity of the two kinds of carbons.

Key Words : AC, BET surface area, SEM, XRD, Photocatalytic activity

Introduction

Activated carbon (AC) and their fibers have been extensively used as adsorbents in industrial technologies related to environmental pollution control due to their well-developed pore structure and excellent adsorption capacity.¹⁻³ Titanium dioxide has also been widely studied as a promising material for environmental protection approach for the past few decades because of its excellent photocatalytic activity. 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 TiO₂ sol,⁷ and mechanical grinding of activated carbon with TiO₂⁸ have been reported for the preparation of carbon/TiO₂ composites. Composite product of activated carbon and TiO₂ 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, activated carbon give very promising for the some kinds of reasons; adsorption and release capability for the pollutants onto the surface of TiO₂, increasing of charge transference between activated carbon and TiO₂ by acidification of surface hydroxyl groups and adsorption of intermediates produced during degradation. We have developed a method for the preparation of activated carbon/TiO₂ composites involving pitch coating of CCl₄ dissolution. The CCl₄ dissolution method is expected to have some advantages due to high diffusivity with homogenous

distribution by non-condensation of pitch in CCl₄ solution.

In this paper, we have prepared to hybrid composite of activated carbon and titanium oxide with synergistic effects by the combined function of adsorptivity and photoactivity. The CCl₄ dissolution method was used pitch/AC/TiO₂ system in order to optimize mixing effects between TiO₂ and AC employed. The pitch used was chosen as the precursor to binding material. The developed catalysts were characterized by BET surface area from adsorption isotherm, 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).

Experimental Section

Materials. A porous and granular AC used in this study was prepared from coconut shell. The coconut shell was pre-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 ACs were washed with deionized water and dried overnight in vacuum dry oven at 683 K. The pitch was used carbon precursor for preparation of the pitch/AC/TiO₂ composite photocatalysts. The granular pitch was supplied from Jungwoo Chemical Co. (Korea). The TiO₂ 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

Table 1. Nomenclatures of Samples Prepared with Different Mixing Ratios of Anatase to AC

Sample	Mixing Ratios	Nomenclatures
Pitch + AC + TiO ₂	15 : 25 : 60	PAT1
	15 : 30 : 55	PAT2
	15 : 35 : 50	PAT3

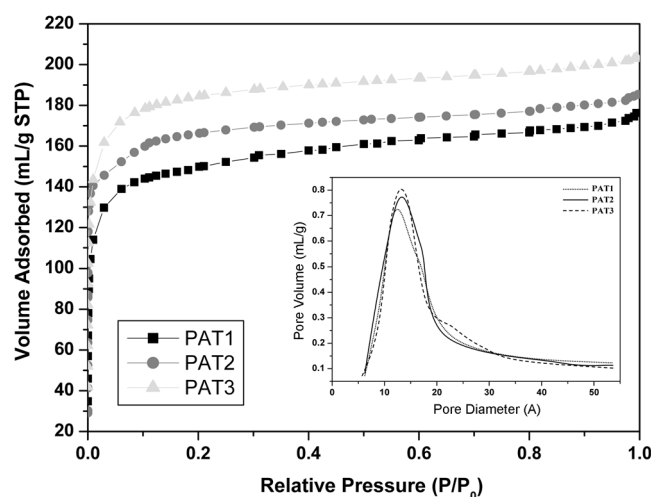
particles of about 30-50 μm . This anatase-type titanium dioxide powder had a relatively large BET surface area about 125 m^2/g . For the melting of pitch, carbon tetrachloride (Dae-Jung Chemical Co., Korea) was used as solvent. After melting of pitch in CCl_4 solution, TiO_2 powder and activated carbon was mixed with pitch- CCl_4 solution. The powder mixtures prepared with different mixing ratios of anatase to AC were heated at 333 K for 1 h. The solvent in the mixtures was vaporized at 353 K for 6 hours. The agglomerates of the pitch/AC/ TiO_2 was heated at 1023 K for 1 h and then crushed at auto miller. The nomenclatures of prepared samples were listed in Table 1.

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 pitch/AC/ TiO_2 composite prepared through the CCl_4 dissolution method. For the elemental analysis in pitch/AC/ TiO_2 , energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with $\text{Cu K}\alpha$ radiation. As one of the analysis of photocatalytic activity, UV/VIS spectrophotometer (Gen-spec III (Hitachi), Japan) was used to characterize of catalytic efficiency of pitch/AC/ TiO_2 composite photocatalysts. Characterization of methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$, MB) in water was determined by the following procedure. A pitch/AC/ TiO_2 powdered sample of 0.05 g was dispersed in an aqueous solution with a concentration of 1.0×10^{-4} 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.

Photocatalytic effect. In order to reveal the photocatalytic effect of the prepared samples, 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 3mL 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.

Results and Discussion

The surface characterizations. Figure 1 shows the adsorption isotherms of N_2 at 77 K and pore size distribution onto the pitch/AC/ TiO_2 composite series. The isotherms

**Figure 1.** Adsorption isotherm of N_2 at 77 K and pore size distribution onto the pitch/AC/ TiO_2 composite series.

presented in this Figure 1 show that the total sorption uptake increases with increasing amount of AC. All of the isotherms were Type I classified with an IUPAC. The formation of micropores can be clearly confirmed by the shape of the isotherms. From the results of the pore size distributions (PSD) calculated for our materials using the density functional theory,⁹ the development of micropores (smaller than 20 \AA) was observed with increasing amount of AC in spite of pore blocking by binder pitch. The textural properties of raw materials and pitch/AC/ TiO_2 composites were shown Table 2. The result of the table demonstrates that there is a slight increase in the BET surface area of composite samples with increasing of the amount of AC. However, almost all surface textural parameters for the composites are a considerably more decrease than that of pristine AC. 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 AC, 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 MB by adsorptivity. Figure 2 depicts SEM micrographs of pitch/AC/ TiO_2 composite samples. It was observed that pitch was covered with AC/ TiO_2 particles. The TiO_2 particles regularly distributed on the around of AC with

Table 2. Textural Properties of Pristine Materials and Pitch/AC/ TiO_2 composite samples

Sample	Parameter			
	S_{BET} (m^2/g)	Micropore Volume (cm^3/g)	Internal Surface Area (m^2/g)	Average Pore Diameter (\AA)
As-received TiO_2	125.0	—	87	—
As-received AC	1829	0.412	1597	17.28
PAT1	728	0.298	572	15.54
PAT2	762	0.310	637	15.83
PAT3	811	0.318	688	16.01

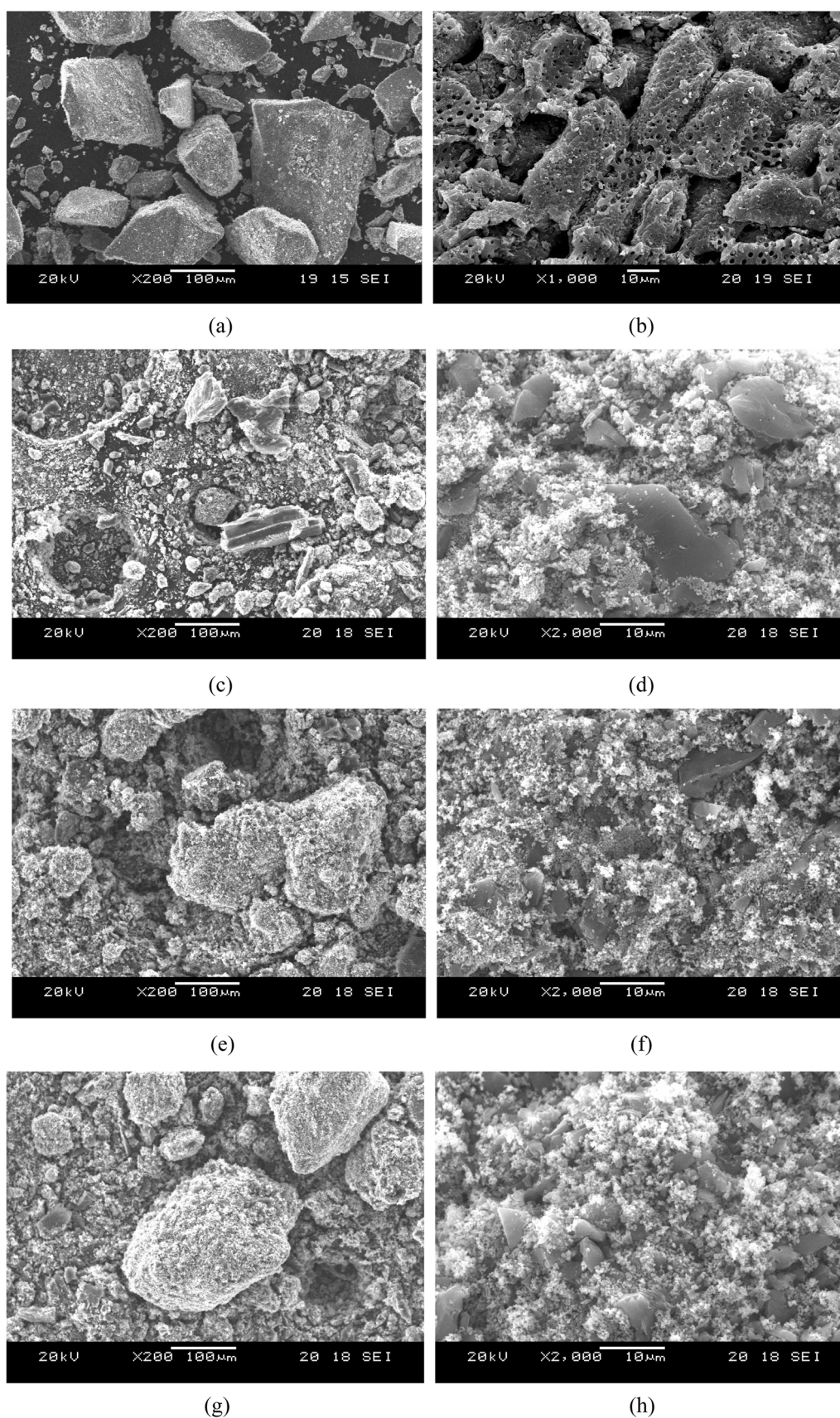


Figure 2. SEM micrographs of pitch/AC/TiO₂ composite prepared with different mixing ratios; (a) raw TiO₂ (×200), (b) pristine AC (×1000), (c) PAT1 (×200), (d) PAT1 (×2000), (e) PAT2 (×200), (f) PAT2 (×2000), (g) PAT3 (×200) and (h) PAT3 (×2000).

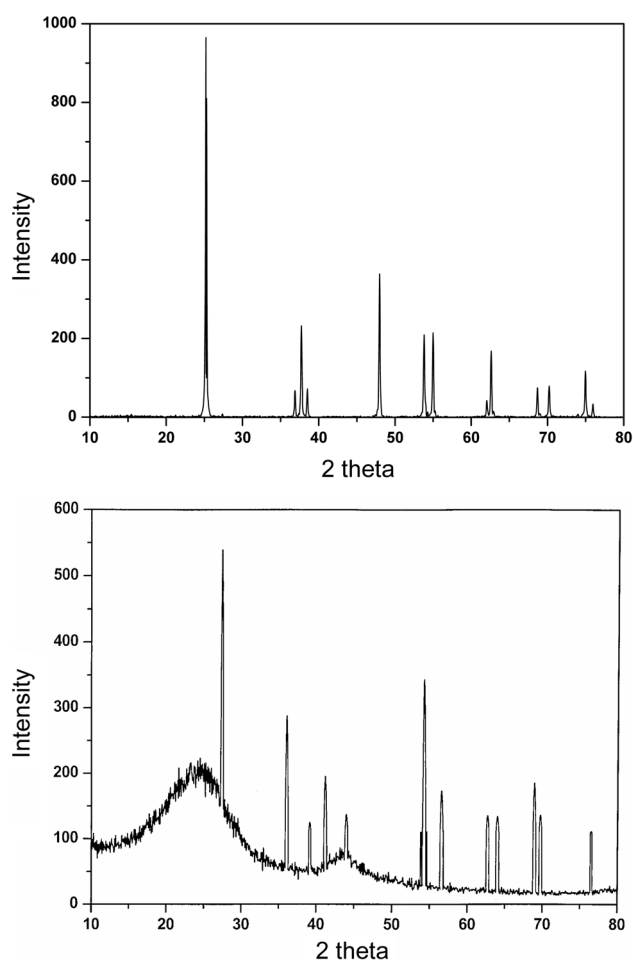


Figure 3. XRD patterns of (a) raw TiO_2 and (b) pitch/AC/ TiO_2 composite heat-treated at 1023 K.

carbon precursor pitch. And some large clusters were found when an amount of AC increases (PAT3). In contrast, homogenous AC and TiO_2 distribution with good particle dispersion was observed when the mixing ratio was 35 : 55 between AC 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 reported¹⁰ 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. Accordingly, high photocatalytic yield were expected for homogenous and small TiO_2 particle distribution (PAT2). Therefore, the higher photocatalytic activity of the sample prepared (PAT2) might be attributed to the homogenous distribution and adsorptivity between TiO_2 and AC produced with binding effect by good pitch dispersion. The TiO_2 particles become pronounced and coarse by pitch treatment and the size of the particles is kept large. On the other hand, many granular particles with regular surface observed as AC/ TiO_2 treated with pitch, which are supposed to be due to the coagulation by pitch as a binder.

Structural and elemental identifications. In Figure 3, changes in XRD pattern are shown on the raw TiO_2 and

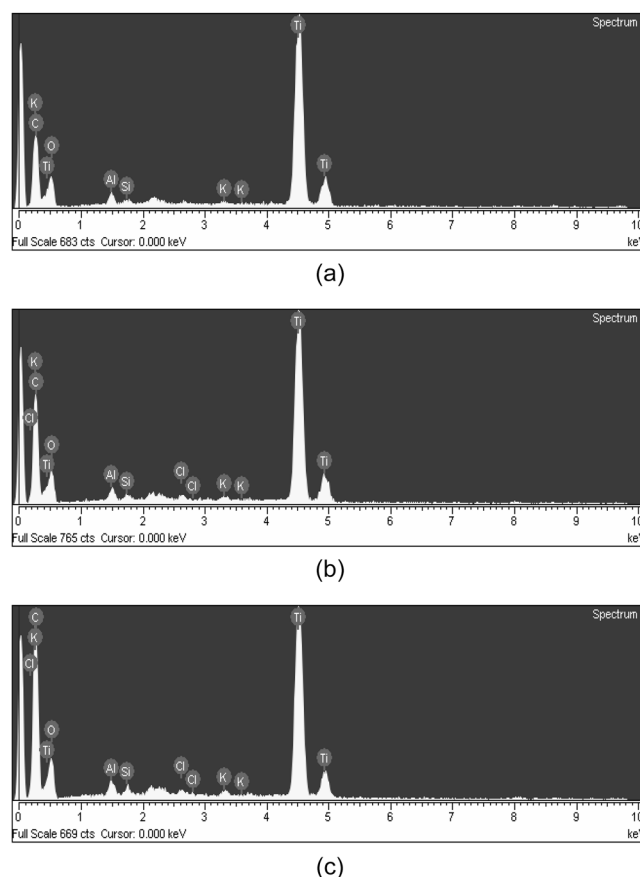


Figure 4. EDX elemental microanalysis of pitch/AC/ TiO_2 composite prepared with different mixing ratios; (a) PAT1, (b) PAT2 and (c) PAT3.

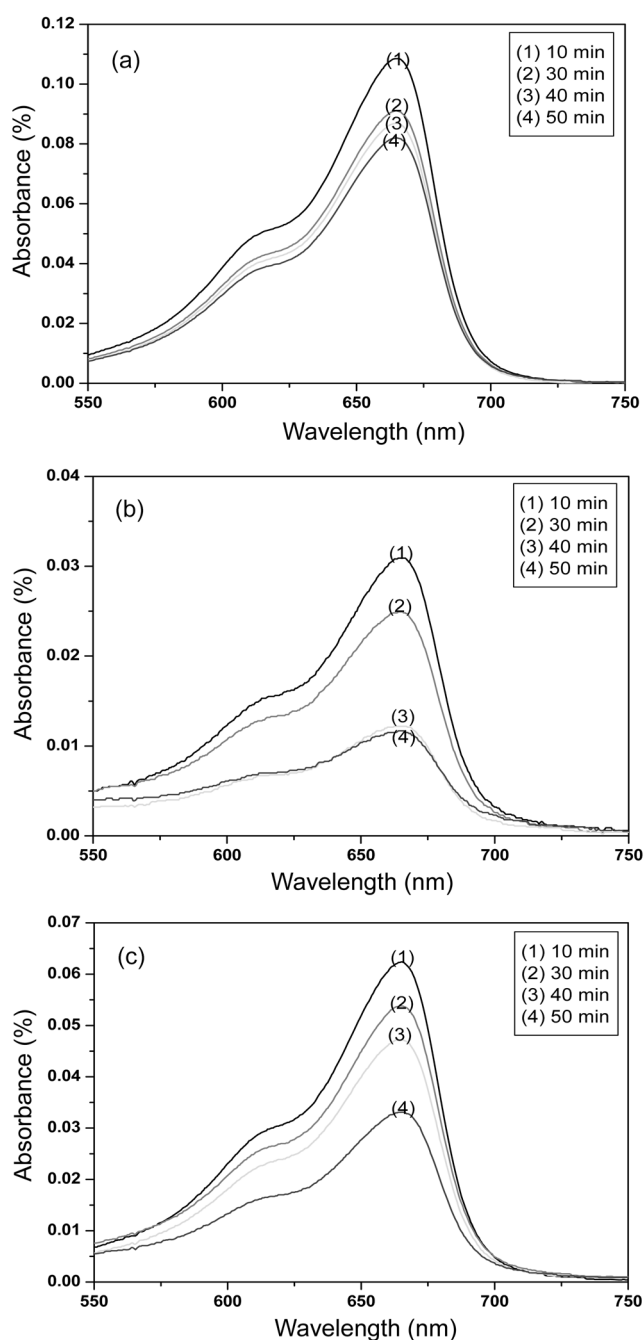
pitch/AC/ TiO_2 composites prepared with heat treatment at 1023 K. Before the heat treatment, TiO_2 structure was shown typical anatase type. After the heat treatment at 1023 K for 1 h, however, the main crystalline phase is transformed to rutile structure. Weak and broad amorphous carbon peaks of grapheme with rutile peaks were observed in the XRD patterns for the pitch/AC/ TiO_2 composites. Even after heat treatment at 1023 K, the anatase phase still remained. 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. In case of pitch/AC/ TiO_2 composites, this is major peaks founded at 27.4, 36.1, 41.2 and 54.3 that belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. It can be concluded that the developed pitch/AC/ TiO_2 composites has a mixture structures between anatase and rutile.

For the elemental microanalysis of the pitch/AC/ TiO_2 composite samples as a function of mixing ratios, these samples were analyzed by EDX. These EDX spectra of pitch/AC/ TiO_2 composites were shown in Figure 4. These spectra show the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and major Ti metal than any other elements. The results of EDX elemental microanalysis of the pitch/AC/ TiO_2 composite

Table 3. EDX Elemental Microanalysis of Samples Prepared with Different Mixing Ratios of Anatase to AC

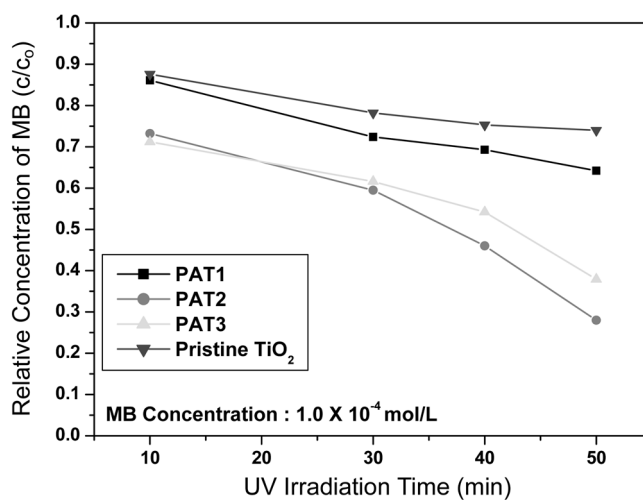
Nomenclatures	C	O	S	Ti	Others
PAT1	31.3	30.1	1.09	36.9	0.56
PAT2	38.6	27.6	0.95	31.9	0.66
PAT3	45.5	26.5	0.84	26.1	0.70

series were listed in Table 3. In the case of most of the samples, carbon and Ti were present as major elements in the pitch/AC/TiO₂ samples. These results were observed for

**Figure 5.** UV/VIS spectra of MB concentration against the pitch/AC/TiO₂ composite under various time conditions; (a) PAT1, (b) PAT2 and (c) PAT3.

each sample show the spectra corresponding to almost all samples rich in C elements with an increase of the amount of AC contents. It should be note that a decrease of the C and S (impure element derived from pitch) content with a increasing of the Ti content is observed for the over all sample series.

Photocatalytic activity. The UV/VIS spectra of MB concentration against the pitch/AC/TiO₂ composites under various time conditions are shown in Figure 5. As can be seen from the spectra, the absorbance maxima for the all samples slowly decrease with increase of UV irradiation time. This implies that the transparent of the MB concentration highly increase by photocatalytic degradation effect of pitch/AC/TiO₂ composites. Figure 6 shows changes in MO concentration under UV light irradiation in the solution. MO removal with pitch/AC/TiO₂ composites photocatalyst is carried out to observe the UV photolysis effect for the MO solution. The changes are plotted on the relative concentration (c/c_0) of MB in the aqueous solution with UV irradiation time for the sample series. It is observed that MO solution is quite unstable with variation of concentration when it is irradiated under UV with pitch/AC/TiO₂ composites, suggesting that the disappearance of MO caused by UV irradiation is presented. The relationship was shown approximately linearity properties depending on irradiation time, as reported on similar modified TiO₂ samples.^{11,12} Because the present of the pitch and AC in pitch/AC/TiO₂ composite samples had a large adsorptivity, as above mentioned, it is believed that the decrease of MB concentration in the aqueous solution can be occurred in two physical phenomena such as adsorption by two kinds of carbons and photocatalytic decomposition by TiO₂. According to earlier study,⁸ MO adsorbed on the AC particles can be eventually degraded by the TiO₂ particles in solution for the case of TiO₂ and AC mixture. This suggests that the TiO₂ deposited on the surface of AC can retain its catalytic activity. The

**Figure 6.** Dependence of relative concentration (1.0×10^{-4} mol/L) of MB in the aqueous solution c/c_0 on time of UV irradiation for the pitch/AC/TiO₂ composite prepared from the different mixing ratios.

synergistic effect has been ascribed¹³ the enhanced adsorption of the pollutants on AC followed by a transfer through an interphase to titania where it is photodegraded. In this study, the excellent photocatalytic activity of the pitch/AC/TiO₂ could be attributed to the homogeneous coated pitch on the external surface by CCl₄ solvent method and excellent adsorptivity of AC. From the removal results of MB in the solution measured periodically over 50 min, the increase in the contents of AC results in a significant degradation effect with decrease of relative concentration (c/c_0) of MB. In case of photocatalytic activity, it was obtained that the curve for PAT2 of the relative concentration (c/c_0) of MB represents lower values than that of PAT3. According to earlier workers,¹⁴ MB molecules absorbed energy from irradiation, thereby shifting their delocalized electrons from bonding to antibonding orbital. Since MB adsorption likely occurs via π - π interactions between its delocalized electrons and the carbon's graphene layers, it is reasonable that shifts in its electron orbitals would alter adsorption. Because the photocatalytic reaction is light excited, carbon deep inside TiO₂ is not easily accessible to light because of enhanced reflection and scattering by the support and the long traveling distance. For the all pitch/AC/TiO₂ composites prepared from different mixing ratios, slope relationship between relative concentration (c/c_0) of MB and UV irradiation time were observed at 1.0×10^{-4} mol/L of MB concentration. From the results between relative concentration (c/c_0) of MB and UV irradiation time, it was observed that removal efficiency of MB for the pitch/AC/TiO₂ composites is better excellent than that of pristine TiO₂ for the all samples. Based on these observations, we therefore can conclude that the decrease of MO concentration should be attributed to the both effects between photocatalysis of the supported TiO₂ and adsorptivity of the two kinds of carbons.

Conclusion

Pitch binded AC/TiO₂ composite photocatalyst was prepared by CCl₄ solvent method with different mixing ratios. Since two kinds of carbons in the particles were porous structure, the pitch binded AC/TiO₂ composites series showed a good adsorptivity and photo degradation activity.

The results of the textural surface properties demonstrate that there are slight increases in the BET surface area and adsorbed volume from adsorption isotherm of composite samples with increasing of the amount of AC. The surface properties of SEM present to the characterization of porous texture on the pitch/AC/TiO₂ composites and homogenous compositions in the particle for all the materials used. From XRD data, a weak and broad carbon peak of graphene remained rutile peaks kept with anatase structure were observed in the X-ray diffraction patterns for the pitch/AC/TiO₂ composites. The EDX spectra for the elemental identification show the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and major Ti metal than any other elements. From the photocatalytic results, the excellent activity of the pitch/AC/TiO₂ composites between relative concentration (c/c_0) of MB and UV irradiation time could be attributed to the both effects between photocatalysis of the supported TiO₂ and adsorptivity of the two kinds of carbons.

References

1. Oh, W. C.; Bae, J. S.; Ko, Y. S. *Carbon Science* **2006**, 7, 105.
2. Oh, W. C.; Lee, H. J.; Bae, J. S. *J. Korean Ind. Eng. Chem.* **2004**, 15, 434.
3. Oh, W. C.; Park, C. S.; Lim, C. S.; Lee, Y. S. *J. Ceramic Processing Research* **2006**, 7, 37.
4. Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. *Chem. Rev.* **1995**, 95, 735.
5. Motos, J.; Laine, J.; Hermann, J. M. *J. Catal.* **2001**, 200, 10.
6. Maldano-Hodar, F. J.; Moreno-Castilla, C.; Rivera-Utrilla, J. *Appl. Catal. A* **2000**, 203, 151.
7. Torimoto, T.; Ito, S.; Kuwabata, S.; Yoneyama, H. *Environ. Sci. Technol.* **1996**, 30, 1275.
8. Motos, J.; Laine, J.; Hermann, J. M. *Carbon* **1999**, 37, 1870.
9. McEnaney, B.; Mays, T. J.; Rouquerol, J.; Rodriguez-Reinoso, F.; Sing, K. S. W.; Unger, K. K. *Characterization of Porous Solids IV*; The Royal Society of Chemistry: 1997; p 604.
10. Graetzel, M.; Frank, A. J. *J. Phys. Chem.* **1982**, 86, 2964.
11. Zhang, X.; Zhou, M.; Lei, L. *Carbon* **2006**, 44, 325.
12. Oh, W. C.; Park, C. S.; Park, C. Y.; Jung, A. R.; Chen, M. L. *Conference Proceeding of Korea Carbon Society* 2006; p 94.
13. Zhang, X.; Zhou, M.; Lei, L. *Carbon* **2005**, 43, 1700.
14. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd Ed.; John Wiley and Sons: 2002; p 224.