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Characterization of composite prepared with different mixing ratios of TiO_2 to activated carbon and their photocatalytic activity

Ming-Liang Chen, Jang-Soon Bae[1], Young-Shin Ko[2] and Won-Chun Oh★

Department of Advanced Materials & Science Engineering, Hanseo University, Chungnam 356-706, Korea
[1]Department of Industrial Chemistry, Dankook University, Chungnam 330-714, Korea
[2]Department of Science Education, Seoul National University of Education, Seoul 137-700, Korea

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Abstract: In this work, pitch/activated carbon/TiO_2 composite were prepared by CCl_4 solvent method with different mixing ratios. The BET surface area of pitch/activated carbon/TiO_2 composite has a significantly increase with increasing activated carbon content in pitch/activated carbon/TiO_2 composite. The surface structure and elemental compositions of the composite were studied by SEM and EDX, respectively. The SEM results were presented to the characterization of porous texture on the pitch/activated carbon/TiO_2 composite. And EDX data was shown the presence of C, O, S, Ti and other elements. The structural properties of the composite were studied in XRD measurements. The TiO_2 crystal phases of the pitch/activated carbon/TiO_2 composite had lots of rutile-type structure which transforms from anatase-type with a little of anatase-type structure. The photocatalytic activities of the composite were evaluated using a photo-decomposition method under UV lamp. The pitch/activated carbon/TiO_2 composites were observed better photocatalytic activity than that of pristine TiO_2.

Key words: Activated carbon, TiO_2, SEM, XRD, EDX, Photocatalytic activity

1. Introduction

Porous carbons have been widely used as adsorbents in technologies related to pollution control due to their well-developed porous texture and excellent adsorption capacity toward pollutants such as NO_x and SO_x. Activated carbon also has experienced widespread use throughout the world and has served as the center of countless discussions focusing on, for example, the role of π-π interactions for the adsorption of aromatics. More recently, the combination of carbonaceous materials with photocatalysts (e.g., TiO_2) has been shown interest and attractive results.[1-5] Because the photocatalyst of titanium oxide has attracted great attention due to its ability to decompose many kinds of contaminants in gas or liquid phase.

Recently, much attention has been paid to the preparation of activated carbon supported TiO_2 photocatalyst because of several reasons[6]: (1) it is easily recovered from the solution; (2) it can be used in the suspension system where a good mixing of the photocatalyst with both light beams and pollutants in water is obtained; (3) activated carbon can concentrate pollutants by adsorption around the loaded TiO_2 leading to an increase in the degradation rate of the

★ Corresponding author
Phone : +82-(0)41-660-1337 Fax : +82+(0)41-688-3352
E-mail: wc_oh@hanseo.ac.kr

pollutants[1,7]; (4) the intermediates produced during degradation can be also adsorbed by activated carbon and then further oxidized to avoid the secondary pollution caused by the intermediates.[8]

The traditional methods used to prepare the supported catalysts were wet impregnation, precipitation, and sol-gel.[9] Recently, metal organic chemical vapor depositions (MOCVD), an extensively used surface coating technology, were applied to the preparation of activated carbon supported catalysts.[10,11]

In the present work, pitch/activated carbon/TiO_2 composites were prepared by CCl_4 solvent method with different mixing ratios. The prepared composites were characterized by BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX) and UV-vis spectrophotometer.

2. Experimental

2.1. Materials

For the melting of pitch, carbon tetrachloride (CCl_4, Daejune Chemicals & Metals Co., Ltd) was used as solvent. Pitch was granular type which was purchased from Jungwoo Chemical Co., Ltd., Korea. The powder type activated carbon (ca. 80 μm) was purchased from Dong Yang Carbon Co., Ltd. The TiO_2 photocatalyst was commercially available (Dukan Pure Chemical Co., Ltd), which was composed of a single phase of anatase with secondary particles of about 80-150 μm aggregated from primary particles of about 30-50 μm. The methylene blue (MB $C_{16}H_{18}N_3S{\cdot}Cl_3H_2O$) was analytical grade which was also purchased from Dukan Pure Chemical Co., Ltd.

2.2. Preparation of pitch/activated carbon/TiO_2 coating

Pitch was melted in CCl_4 solution completely, and then titanium oxide powder and activated carbon powder put into the pitch-CCl_4 solution. The prepared mixing solution was stirred and melted by using a Hot plate & stirrer (DMS Co., DS-201HS, Korea) at 343-353 K. After the CCl_4 solution was completely evaporated, the obtained mixture was subjected to heat treatment at 1023 K for 1 h. In this experiment, the composite was prepared as different mixing ratios with pitch, activated carbon and TiO_2. *Table* 1 was shown the information about the different mixing ratios of pitch/activated carbon/TiO_2 composite.

Table 1. Nomenclatures of Prepared Samples with Different Mixing Ratios of Anatase TiO_2 to Activated Carbon

Sample	Mixing Ratios	Nomenclatures
Pitch +Activated Carbon + TiO_2	15 : 25 : 60	PAT1
	15 : 30 : 55	PAT2
	15 : 35 : 50	PAT3

2.3. Characterization

For the physical parameter measurements, nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics, USA) at 77 K. For observation of the surface state and structure of TiO_2 transformed through the pitch/activated carbon treatment, the morphology of the pitch/activated carbon/TiO_2 composite was studied by a scanning electron microscope (SEM, JSM-5200 JOEL, Japan). The crystal structure of TiO_2 was identified by X-ray diffraction (XRD, Shimatz XD-D1, Japan). The elemental analysis of pitch/activated carbon/TiO_2 composite was measured by energy dispersive X-ray analysis (EDX).

2.4. Photocatalytic degradation of methylene blue(MB)

The photocatalytic effectiveness of pitch/activated carbon/TiO_2 composite was determined under an ultraviolet (UV) lamp (356 nm, 1.2 mW/cm^2). The initial concentration of MB was $5{\times}10^{-5}$ mol/L. At this time the concentration of MB in the solution was denoted as C_0. The amount of the composite which put into the MB solution was 0.05 g. After the composite put into the MB solution, the UV light was turned on. And then the solution was irradiated for 10 min, 30 min, 40 min, and 50 min. The concentration of MB after photo-degradation by TiO_2 reaction (C) was determined by using a UV-vis spectrophotometer (660 nm, Genspec III (Hitachi), Japan).[12]

3. Results and Discussion

3.1. Physical properties of pitch/activated carbon/TiO_2 composite

The BET surface area for pitch/activated carbon/TiO_2 composite prepared at 1023 K give a common dependence on activated carbon content. *Table* 2 shows the textural properties of TiO_2, activated carbon and pitch/activated carbon/TiO_2 composite. Examination of the table demonstrates that there is significant increases in the BET surface area of pitch/activated carbon/TiO_2 with increasing activated carbon contents in the composite. However, micropore volumes were slightly increased with increasing C contents. It was very difficult to evaluate the surface area of TiO_2 particles and carbon layer in the composite, separately. According to the former study,[13] carbon-coated anatase powders were reported photocatalytic activity for methylene blue decomposition in aqueous solution and more pronounced adsorption of methylene blue than anatase powders without carbon coating. Methylene blue (MB), with a critical pore dimension of 15 Å is expected to experience optimal adsorption by a carbon with comparable pore sizes.[14] Applying to the data shown in the *Table* 2, it can be observed that the PAT1, PAT2, and PAT3, with that average pore diameter is 15.54 Å, 15.83 Å, and 16.01 Å, respectively, and demonstrate great uptake of MB aqueous solution.

In *Fig.* 1, the changes in morphology of the particles with heat treatment at 1023 K show on three samples, PAT1, PAT2, and PAT3, respectively. The SEM pictures provide information about the distribution of pitch on the activated carbon/TiO_2 surface. *Fig.* 1 (a) and (b) were shown the microphotographs of PAT1. It can be clearly seen that pitch was coated with activated carbon/TiO_2 particles. The microphotographs of PAT2 and PAT3 were shown in *Fig.* 1 (c), (d) and (e), (f), respectively. It was presented that the amount of activated carbon in the samples was increased and the samples look like increase of porosity. A homogeneous distribution of activated carbon with providing the large surface area can be promoting the photocatalytic efficiency for the removal of MB in aqueous solution. It will have to be taken into account for further analysis of the removal of MB in aqueous solution because large surface strongly influences both the adsorption capacity and the photocatalytic activity for MB aqueous solution.

For the elemental microanalysis of pitch/activated carbon/TiO_2 composite as a function of mixing ratios, these composites were analyzed by EDX. *Table* 3 contains the elemental parameters deduced from an analysis of the EDX. The examination of the table was demonstrated that the presence of C, O, S, Ti and other elements. All of the composites were richer in carbon and Ti metal than any other elements. It was also demonstrated that the amount of Ti is decreased and the amount of carbon is increased by following the order of PAT1, PAT2 and PAT3 in the Table 3.

Fig. 2 depicts XRD patterns of (a) pristine TiO_2 and (b) pitch/activated carbon/TiO_2 composite heat treated at 1023 K. It was clearly seen that rutile TiO_2

Table 2. Textural Properties of Pristine Materials and Pitch/Activated Carbon/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 (Å)
As-received TiO_2	125.0	-	87	-
As-received Activated Carbon	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

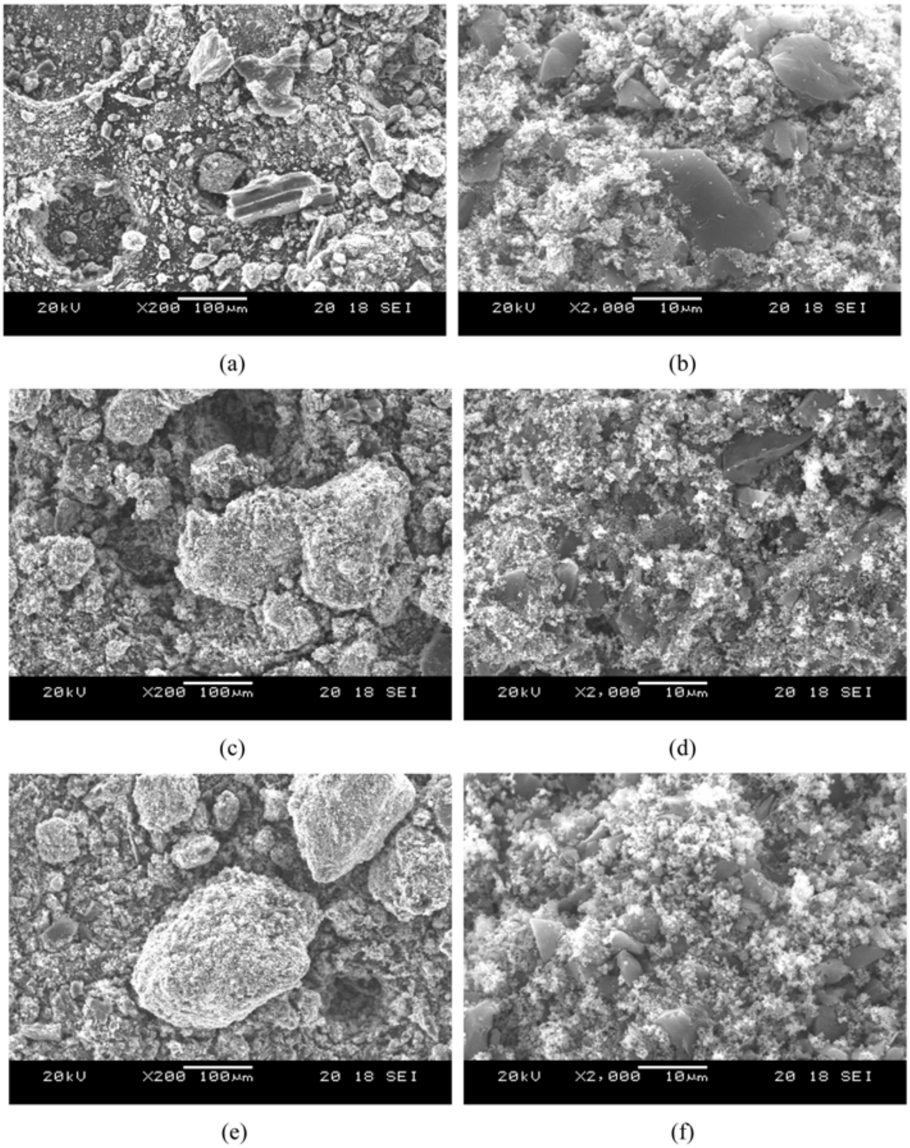

Fig. 1. SEM microphotographs of pitch/activated carbon/TiO_2 composite prepared with different mixing ratios; (a) PAT1 (×200), (b) PAT1 (×2000), (c) PAT2 (×200), (d) PAT2 (×2000), (e) PAT3 (×200) and (f) PAT3 (×2000).

Table 3. EDX Elemental Microanalysis of Prepared Samples with Different Mixing Ratios of Anatase TiO_2 to Activated Carbon

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

is obtained mainly and a little of anatase appear in the pitch/activated carbon/TiO_2 composite as compared to *Fig.* 2 (a) and (b), suggesting the heat-treatment temperature has much effect on the crystal structure of TiO_2. It was reported that,[2] the anatase phase formed below 773 K starts to transform to rutile-type structure above 873 K and changed into a single phase of rutile at 973 K-1173 K, and in general, it is also known that anatase-type have great photocatalytic activity, and the photocatalytic activity is the greatest when the mixing ratios of anatase

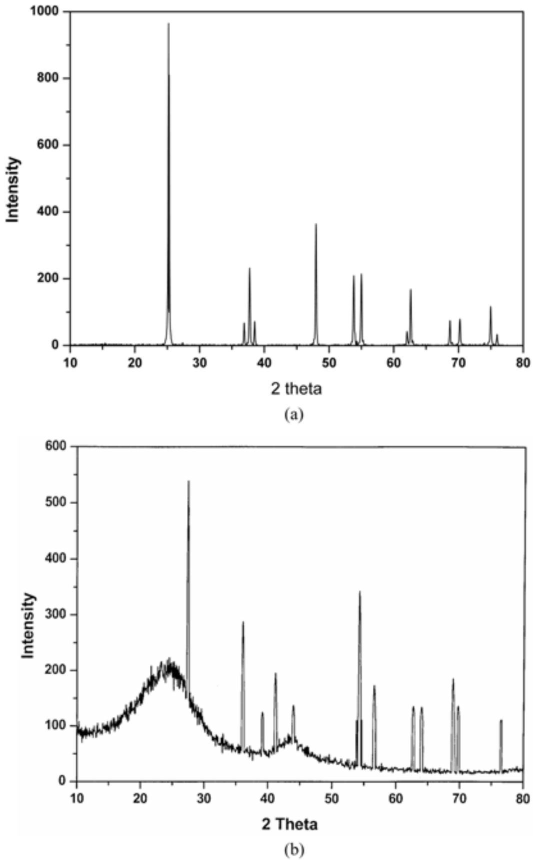

Fig. 2. XRD patterns of (a) pristine TiO_2 and (b) pitch/activated carbon/TiO_2 composite heat-treated at 1023 K.

and rutile is 3:1. In our case, it can be concluded that the developed pitch/activated carbon/TiO_2 composite has a mixture structures between anatase and rutile. The weak and wide patterns of carbon are also seen in the *Fig.* 2(b), so it can be known that the carbon was existent in the pitch/activated carbon/TiO_2 composite.

3.2 Photocatalytic activity of pitch/activated carbon/TiO_2 composite

Fig. 3 was shown the absorbance of pitch/activated carbon/TiO_2 composite prepared with different mixing ratios on MB solution concentration of 5×10^{-5} mol/L under UV irradiation after 10 min, 30 min, 40 min, and 50 min. In *Fig.* 3 (a), it can be seen that the absorbance of PAT1 under UV irradiation after 10 min was the highest, after 30 min and 40

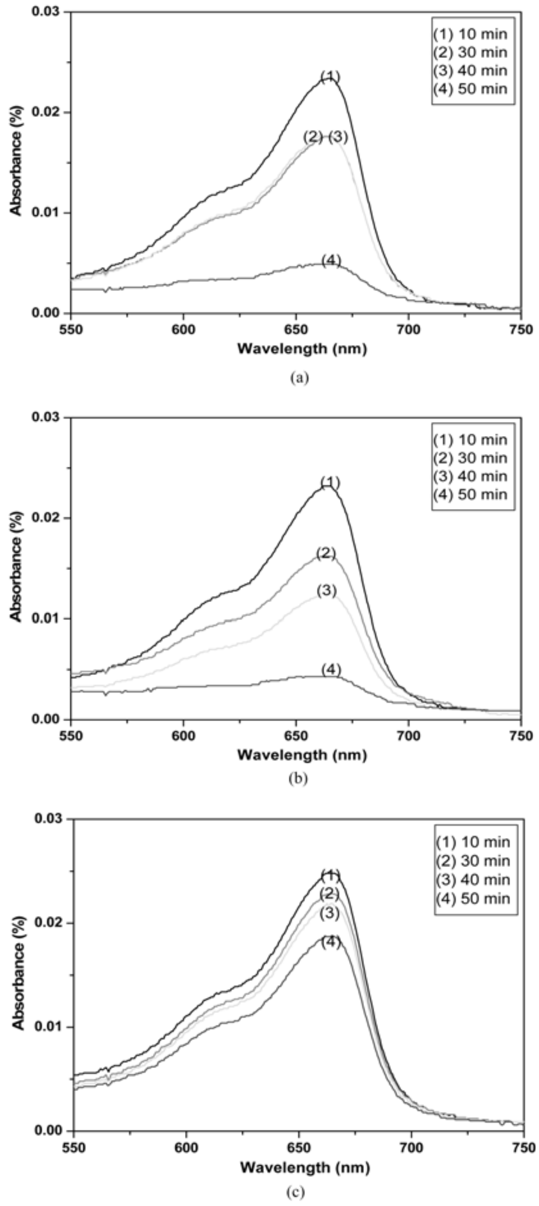

Fig. 3. UV-vis diffuse reflectance spectra of pitch/activated carbon/TiO_2 composite on methylene blue (MB) solution concentration of 5.0×10^{-5} mol/L; (a) PAT1, (b) PAT2, (c) PAT3.

min were identical, and after 50 min was the lowest. The absorbencies of PAT2 and PAT3 under UV irradiation were shown in *Fig.* 3 (b) and (c), respectively. It was demonstrated that the absorbencies of PAT2 and PAT3 were decreased by following the order of UV irradiation time with 10 min, 30 min, 40

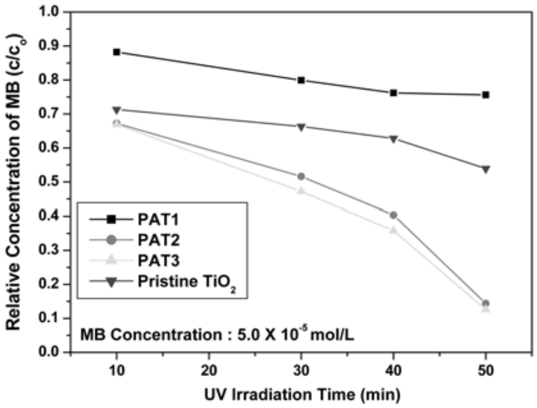

Fig. 4. Dependence of relative concentration of MB in the aqueous solution c/c$_0$ on time of UV irradiation for the pitch/activated carbon/TiO$_2$ composite prepared from the different mixing ratios; the concentration of MB: 5.0×10^{-5} mol/L.

min and 50 min.

Fig. 4 was shown the comparison of the photocatalytic activity of the pristine TiO$_2$ and the pitch/activated carbon/TiO$_2$ composite prepared with different mixing ratios in MB concentration of 5×10^{-5} mol/L under UV irradiation in the solution. The photocatalytic activity of the pristine TiO$_2$ was better than that of PAT1, but the photocatalytic activity of PAT2 and PAT3 were better than that of the pristine TiO$_2$ and PAT1. Because of the photocatalytic activity of anatase-type TiO$_2$ was better than that of rutile-type TiO$_2$. However, so it was mainly expressed the adsorption capacity of activated carbon in the PAT2 and PAT3. These results were as the same as the results that Ahuja[15] indicated, the increasing of BET surface area was important reason of the increasing of photocatalytic activity of carbon/TiO$_2$.

4. Conclusions

As one of the new method by using carbon tetrachloride solvent the pitch/activated carbon/TiO$_2$ composite with photocatalytic activity and high adsorption capacity has been characterized. The BET surface area was increased with the increasing of activated carbon contents, which was made by changing the mixing ratios of the activated carbon with pristine TiO$_2$. The SEM results present to the characterization of surface properties on the pitch/activated carbon/TiO$_2$ composite and a homogeneous distribution of pitch on activated carbon and TiO$_2$ provided with the large surface area. From XRD data, a weak and broad carbon peak with lots of rutile and a few of anatase peaks were observed in diffraction patterns for the pitch/activated carbon/TiO$_2$ composite. The EDX spectra show the presence of C, O, S, Ti and other elements. It was observed that all of these composites were richer in carbon and Ti metal than any other elements. Finally, from the comparison of the photocatalytic activity of the pristine TiO$_2$ and the pitch/activated carbon/TiO$_2$ composite prepared with different mixing ratios in MB concentration of 5×10^{-5} mol/L under UV irradiation in the solution. It can be shown that the photocatalytic activity of PAT2 and PAT3 was more excellence than that of the PAT1 and pristine TiO$_2$.

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