Characterization of Fe-ACF/TiO₂ composite Photocatalysts Effect Via Degradation of MB Solution

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Fe-ACF/TiO₂ 복합체의 특성과 MB용액의 분해에서 포토-펜톤 효과
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ABSTRACT: In this paper, the Fe-activated carbon fiber (ACF)/TiO₂ composite catalysts were prepared by a sol-gel method. The synthesized photocatalysts were used for the photo degradation of Methylene blue solution under UV light. From Brunauer-Emmett-Teller measurements (BET) data, it was shown the blocking of the micropores on the surface of ACF by treatment of Fe and Ti compound. As shown in SEM images, the ferric compounds and titanium dioxides were fixed onto the ACF surfaces. The result of X-ray powder diffraction showed that the crystal phase contained a mixing anatase and rutile structure and the 'FeO+TiO₂' from the composites. The EDX spectra for the elemental analysis showed the presence of C, O, and Ti with Fe peaks. Degradation activity of MB could be attributed to -OH radicals derived from electron/hole pair's reactions due to photolysis of TiO₂ and photo-Fenton effect of Fe.


Keywords: Activated carbon fiber; Fe; Methylene blue; photo-Fenton; SEM.

I. Introduction

In the past decades, the photocatalytic oxidation of organic dyes and pollutants in the waste water by semiconductor photocatalyst TiO₂ has been extensively studied.1-5 It has been considered a promising material for environmental treatment, because it is stable, non-toxic, anti-oxygen oxidation, complete mineralization, and no secondary pollution.6,5 But the photocatalytic activity of TiO₂ has high electron/hole pairs recombination rate and low interface area. Rapid recombination of electron/hole pairs can be reduced to hv reaction, and product of electron/hole pairs were decreased by low interface area.

\[
\text{TiO}_2 + \text{hv} \rightarrow h_{b}^+ + e^- \]

h_{b}^+ + H₂O \rightarrow \cdot \text{OH} + \text{H}^+ \]

So many reports have focused on adding some transition metal elements in TiO₂ in order to amend above defects. In recent years, metallic components such as Ni,9,13 Zn,14-15 Zr16-17 and Fe18 have been successfully treated with TiO₂ for obtaining good photocatalytic effect. Among these researches, enhancement of photocatalytic efficiency of Fe doped TiO₂ has been proved, because it can reduce recombination rate of electron/hole pair and produce photo-Fenton reaction. by photo-Fenton process producing -OH radicals.

\[
\text{Fe}^{3+} + \cdot \text{OH} + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{OH} \]

Thus, iron widely has been applied in photo catalytic reaction. But it was reported that the larger amounts of containing Fe³⁺ can inhibit the photocatalytic activity,19-20 which was considered that electron/hole pairs were digested by different spe-
cies of iron ion. Therefore, appropriate amount of Fe added into composite catalysts can enhance the photocatalytic activity. Moreover, activated carbon fiber (ACF) is highly microporous, having a high surface area, a larger pore volume and a uniform microspore size distribution. TiO$_2$ particle could be easily fixed on ACF surface and thus have improved defects at low interface area. Thus, ACF/TiO$_2$ composites are typically used to obtain the combined effects of the photo activity. Therefore, combination of ACF and TiO$_2$ with Fe could remarkably increase the photocatalytic activity.

In this study, Fe-ACF/TiO$_2$ composite was obtained by porous ACF, the TiO$_2$ was derived from titanium (IV) oxysulfate hydrate (TiOSO$_4$•xH$_2$O (TOS), Sigma-Aldrich, Germany), and Fe (NO$_3$)$_3$ solution employed a sol-gel method. The prepared composites were characterized by BET, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX). Then, it was suggested that the experimental preparations of Fe-ACF/TiO$_2$ composites were based on the control of amounts of Fe and Ti. The degradation effects of MB dye under UV light were investigated using the prepared Fe-ACF/TiO$_2$ composites.

II. Experimental

1. Materials

ACFs were obtained from EAST ASIS Carbon Fibers Co., (Ltd, AnShan, China) and their properties are shown in Table 1. Ten grams of ACFs were added into 50 ml of 0.1, 0.25 and 0.5 M Fe (NO$_3$)$_3$ solutions, respectively, and stirred for 24 h at room temperature. The Fe (NO$_3$)$_3$•9H$_2$O was purchased from Duksan Pure Chemical Co. (99+%, ACS reagent, Korea). Five grams of Fe-ACF composites heated at 773K for 1 h were added into different volume (15 ml, 20 ml) of 0.1 M TOS solutions and stirred for 5 h in air atmosphere. The mixtures were vaporized at 373 K, and then heated at 923 K for 1 h. After cooling, the Fe-ACF/TiO$_2$ composites were obtained. The nomenclatures and preparation procedures of the samples are listed in Table 2.

<table>
<thead>
<tr>
<th>Preparation process</th>
<th>Nomenclatures</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="773K">ACF + 0.1M Fe(NO$_3$)$_3$</a> + 0.1M TOS/alcohol 15ml](923K)</td>
<td>F1T1</td>
</tr>
<tr>
<td><a href="773K">ACF + 0.1M Fe(NO$_3$)$_3$</a> + 0.1M TOS/alcohol 20ml](923K)</td>
<td>F1T2</td>
</tr>
<tr>
<td><a href="773K">ACF + 0.25M Fe(NO$_3$)$_3$</a> + 0.1M TOS/alcohol 15ml](923K)</td>
<td>F2T1</td>
</tr>
<tr>
<td><a href="773K">ACF + 0.25M Fe(NO$_3$)$_3$</a> + 0.1M TOS/alcohol 20ml](923K)</td>
<td>F2T2</td>
</tr>
<tr>
<td><a href="773K">ACF + 0.5M Fe(NO$_3$)$_3$</a> + 0.1M TOS/alcohol 15ml](923K)</td>
<td>F3T1</td>
</tr>
<tr>
<td><a href="773K">ACF + 0.5M Fe(NO$_3$)$_3$</a> + 0.1M TOS/alcohol 20ml](923K)</td>
<td>F3T2</td>
</tr>
</tbody>
</table>

2. Characterization and investigation for the samples

To characterize the Fe-ACF/TiO$_2$ prepared, the BET surface area by N$_2$ adsorption method was measured at 77 K using a BET analyzer (MONOSORB, USA). The surface and structure of the Fe-ACF/TiO$_2$ composites were observed using a SEM (JSM-5200, Japan). The crystalline phases were analyzed using XRD (Shimadz XD-D1, Japan) with Cu K$_\alpha$ radiation. For the elemental analysis of the Fe-ACF/TiO$_2$ composites, EDX spectra were also obtained. For the measurement of photo-degradation effects, MB was degraded via the following procedure. A Fe-ACF/TiO$_2$ powdered sample of 0.03 g was added into a concentration of 1.0 × 10$^{-5}$ mol/L in a dark atmosphere at room temperature. Each concentration was measured as a function of UV irradiation time. Results were recorded using a Genspec III (Hitachi, Japan) spectrometer.

3. Photocatalytic activity

Fe-ACF/TiO$_2$ photocatalysts was used to degrade MB in aqueous media under ultraviolet light irradiation. For UV irradiation, the reaction tube was placed in the darkness box. The UV lamp was located at the distance of 100 mm from the solution in darkness box. After irradiation at 10 min, 30 min, 60 min, 90 min, and 120 min, the samples were extracted...
from the reactor and 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 UV wavelength line of 220 and 800 nm.

III. Results and discussion

1. The surface characteristics

The Fe-ACF/TiO$_2$ catalysts prepared with different concentrations of Fe and different volumes of TOS solution were named as F1T1, F1T2, F2T1, F2T2 and F3T1, F3T2. These BET surface areas are summarized in Table 3. From the results shown, it can be clearly seen that the specific surface area was gradually decreased by increasing the Fe and Ti contents into Fe-ACF/TiO$_2$ composites. Generally, the BET surface area is considered to be decreased due to the blocking of the micropores by surface complexes introduced through the formation of the Fe-ACF/TiO$_2$ composites.$^{18}$ The variation of surface parameters is attributed to the increase of the amount of TiO$_2$ and Fe components. The similar phenomena has also been observed in the references.$^{21-22}$

The SEM images of Fe-ACF/TiO$_2$ composites are shown in Figure 1. The TiO$_2$ particles are fixed on the surface of ACF from Figure 1 observations, although the particles were partially agglomerated. In comparison of the amounts of Fe and Ti in all samples, we can find same results. Generally, it is considered that good dispersion of particles can produce high photocatalytic activity. In previous studies,$^{23-24}$ ACF/TiO$_2$ composites were prepared with nitric acid in order to enhance the homogenous and uniform distribution of TiO$_2$ particles. The SEM images showed that the TiO$_2$ particles on the Fe-ACF surfaces are not evenly distributed in all types of the Fe-ACF/TiO$_2$ composites. Although we could not clearly find out Fe particles in SEM images of Fe-ACF/TiO$_2$ composites, maybe the size of the Fe particle was estimated very small, but it was confirmed in XRD and EDX results.

2. Crystal structure and elemental analysis

Figure 2 shows the XRD results of Fe-ACF/TiO$_2$. Diffraction peaks corresponding to anatase and rutile phase are marked with 'A' and 'R'. And, the diffraction peaks corresponding to 'FeO+TiO$_2$' and 'γ-Fe$_2$O$_3$' phase are marked with 'F' and 'O', respectively. XRD patterns of the composites presented that the Fe-ACF/TiO$_2$ composites consisted of a mixed phases as anatase and rutile phase. The anatase phase was obtained after heat treatment at 773K. The main diffraction peaks at 25.3, 37.8, 48.0, 53.8 and 62.5 are diffractions of (101), (004), (200), (105) and (204) planes of anatase. However, the diffraction peaks of rutile phase were minorly appeared in this figs, the phase transition can be attributed to formation of pure oxides due to high temperature at 973 ~1173 K.$^{25}$ But phase transition temperature has been shown to depend on impurity contents, particle size and surface area.$^{26-28}$ The similar phenomena has also been observed in the references.$^{29-30}$

Moreover, we can clearly find the peaks of 'FeO+TiO$_2$' for all of these samples in the XRD patterns. It is noteworthy that the 'FeO+TiO$_2$' peaks in F3T1 and F3T2 show very higher than that of other samples. As expected, the intensity of 'FeO+TiO$_2$' peaks increased with an increase of concentration of Fe source in the solution. Diffraction peaks of 'γ-Fe$_2$O$_3$' are only found in F3T1 and F3T2, the main diffraction peaks have characteristic reflections of (110), (210), and (211).$^{31}$ These nanocrystallites were produced by solvothermal reaction and heat treatment at 773-1173 K.$^{32}$

Figure 3 shows the element analysis of Fe-ACF/TiO$_2$. From the spectra, all of the Fe-ACF/TiO$_2$ composites show the main peaks of O, Ti and Fe. The numerical results are listed in the Table 4. The amounts of Fe and Ti element were clearly affected on the different samples. As expected, the contents of Fe element in the composites increased with the increase of Fe (NO$_3$)$_3$ concentrations. Similarly, the contents of Ti element in the composites increased with the volume of TOS solution increased. However, the amount of Ti element is greatly different values among F1T2, F2T2 and F3T2. It can be explained that the Fe and TiO$_2$ particles on the complexes were partially agglomerated on ACF surface from their SEM images.

Table 3. Specific BET surface areas of Fe-ACF/TiO$_2$ composite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
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<tbody>
<tr>
<td>F1T1</td>
<td>682</td>
</tr>
<tr>
<td>F1T2</td>
<td>638</td>
</tr>
<tr>
<td>F2T1</td>
<td>660</td>
</tr>
<tr>
<td>F2T2</td>
<td>539</td>
</tr>
<tr>
<td>F3T1</td>
<td>509</td>
</tr>
<tr>
<td>F3T2</td>
<td>302</td>
</tr>
</tbody>
</table>

Table 4. EDX elemental microanalysis of Fe-ACF/TiO$_2$ composites.

<table>
<thead>
<tr>
<th>Sample (wt. %)</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1T1</td>
<td>67.45</td>
<td>19.08</td>
<td>9.16</td>
<td>2.04</td>
</tr>
<tr>
<td>F1T2</td>
<td>66.53</td>
<td>19.09</td>
<td>9.69</td>
<td>2.58</td>
</tr>
<tr>
<td>F2T1</td>
<td>63.16</td>
<td>22.23</td>
<td>7.59</td>
<td>4.72</td>
</tr>
<tr>
<td>F2T2</td>
<td>59.45</td>
<td>19.03</td>
<td>11.63</td>
<td>6.33</td>
</tr>
<tr>
<td>F3T1</td>
<td>59.78</td>
<td>19.37</td>
<td>8.16</td>
<td>9.57</td>
</tr>
<tr>
<td>F3T2</td>
<td>46.98</td>
<td>26.23</td>
<td>15.29</td>
<td>8.71</td>
</tr>
</tbody>
</table>
Figure 1. SEM images obtained from powdered Fe-ACF/TiO$_2$ composites: (a) F1T1, (b) F1T2, (c) F2T1, (d) F2T2, (e) F3T1 and (f) F3T2
3. The photocatalytic activity of Fe-ACF/TiO$_2$ composites

Figure 4 shows degradation efficiency of six kinds of photocatalysts against MB solutions under the same concentrations. And UV/Vis spectra of MB degradation are obtained at condition of five different irradiation times. For the comparison of degradation curves, the absorption peaks at around 250 nm are shown in Figure 4 (a) (b) (c) and (d). The unique and sharp peak was confirmed that degradation product of MB molecule possessed same compound. Because initial solution only contained single organic compound, so the compound can be considered simple phenyl compounds from UV spectra. In Figure 4 (e) and (f), absorption maximum peaks were shifted to 660 nm area. It means not simultaneously degradation of the nitrogen substituent on aromatic compounds as well as...
Figure 4. UV/Vis spectra of MB concentration against the Fe-ACF/TiO$_2$ composite under various time conditions: (a) F1T1 (b) F1T2 (c) F2T1 (d) F2T2 and (e) F3T1 (f) F3T2.
Figure 5. Dependence of relative concentration of MB in the aqueous solution ln Abs (max)/Abs(max)0 on UV irradiation time for the Fe-ACF/TiO2 composites.

Figure 6. Product of \( \cdot \text{OH} \) radicals by photolysis of TiO2 and photo-Fenton of Fe reactions.

MB molecules. It showed that the MB solution was not completely degraded by the composites of F3T1 and F3T2. It is also shown that photocatalytic activity of F3T1 and F3T2 were observed lower than that of other samples. Furthermore, another sharp absorption peak was found out at around 339 nm in Figure 4 (c) and (d). It is considered that this red shifted phenomenon was attributed to degradation product containing other substituent on aromatic compounds. According to above results, it was noteworthy that the photocatalytic activity was different with introducing different amounts of Fe or Ti components.

Figure 5 shows a comparison of photocatalytic efficiency. As shown in the figure, different content of Fe was added into two series of samples which named as F1T1, F2T1, F3T1 and F1T2, F2T2, F3T2, respectively, we can find out F2T1 and F2T2 were the best in each series. It can be considered that \( \cdot \text{OH} \) radicals contained as high concentration in samples of F2T1 and F2T2. The proposed reactions are shown in Figure 6. We clearly have seen that higher concentration of Ti or Fe compounds can produce higher amount of \( \cdot \text{OH} \) radicals. Therefore, photocatalytic activity of F2T1 was better than that of F1T1. But, the activity of F2T2 photocatalysts was better than that of F1T2 due to the increase of concentration of Fe. However, photocatalytic activity of F2T1 was better than that of F1T1. Finally, the activity of F2T2 was better than that of F2T1 due to the increase of concentration of Ti components. However, photocatalytic activity of F3T1 and F3T2 were lower than that as expect of any other cases with the increase of concentration of Fe. It was attributed to that superfluous of Fe was comprised in samples of F3T1 and F3T2. The Fe\(^{3+} \) becomes recombination centers resulting in consumed electron/hole pairs and reduced photo-Fenton reaction due to the increase of the amounts of Fe concentration.\(^3\)

The proposed reactions were showed in the equations ((1)-(5)):

\[
\begin{align*}
\text{TiO}_2 + \nu & \rightarrow h^+ + e^- \quad (1) \\
\text{Fe}^{2+} + h^+ & \rightarrow \text{Fe}^{3+} \quad (2) \\
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \quad (3) \\
\text{Fe}^{3+} + h^+ & \rightarrow \text{Fe}^{4+} \quad (4) \\
\text{Fe}^{4+} + e^- & \rightarrow \text{Fe}^{3+} \quad (5)
\end{align*}
\]

From above reactions, the increase of iron ion concentration was one reason of electron/hole pairs recombination. This recombination was brought by TiO2 surface, which can be controlled by different concentration of iron ion due to the decrease of photo-Fenton effect. Consequently, photocatalytic activity was reduced.

As expected, when the amount of Fe was deficient in samples of F1T1, F1T2, F2T1 and F2T2, photocatalytic activity was enhanced with the increase of Ti and Fe components. It was considered that a large numbers of \( \cdot \text{OH} \) radicals were one reason of MB degradation. In comparison of F3T1 with F3T2, when samples possess high concentration of Fe, photocatalytic activity was on the contrary reduced with the increase of amount of Ti component. This result was shown that much electron/hole pairs were consumed by iron ion. It means electron/hole pairs were deficient in MB solution before the increase of the amount of Ti components. When the amount of electron/hole pairs was less than iron ion dissipative amount, equations ((2)-(5)) were more continually happened with the increase of the amounts of Ti components. The photo-Fenton reaction of Fe was decreased, so the amount of \( \cdot \text{OH} \) radical decreased with the increase of Ti component. Therefore, photocatalytic activity was not enhanced with the increase of Ti component. Consequently, if the amount of electron/hole pairs and dissipation of iron ion is equivalent, photocatalytic activity would be increased with the increase of Ti component by controlling of the ratio of Fe and Ti in composites.
Composites of Fe-ACF/TiO₂ were successfully synthesized from Fe-ACF and TiO₂ by a sol-gel method. The BET surface area for Fe-ACF/TiO₂ composites decreased with the increase of TiO₂ and Fe components. From the SEM results, the TiO₂ particles were irregularly dispersed on ACF surface. In the area for Fe-ACF/TiO₂ composites decreased with the increase from Fe-ACF and TOS by a sol-gel method. The BET surface of TiO₂ and Fe components. From the SEM results, the TiO₂ patterns of 'FeO+TiO₂' are clearly observed with anatase and rutile phases. The EDX spectra showed that the main elements such as C, O, Ti and Fe were existed. According to the photocatalytic results, photocatalytic activity was affected by radical, deficient content of Fe can produce more OH radical and enhanced photocatalytic activity, which can be enhanced with an increase of Ti composition. When the amount of Fe was superfluous, photo-Fenton reaction of Fe was restrained and photocatalytic activity of Fe-ACF/TiO₂ composite was decreased with amount of Ti.

References