Comparative Analysis of the Physical Properties and Photocatalytic Effects for C/TiO₂ Complexes Derived from Titanium n-butoxide

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Abstract

The hybrid C/TiO₂ complexes were prepared by a method involving the penetration of titanium n-butoxide (TNB) solution with porous carbons. The photocatalysts were investigated for their surface textural properties and SEM morphology, structural crystallinity and elemental identification between porous carbon and TiO₂, and dye decomposition performance. For all the C/TiO₂ complexes prepared by TNB solution methods, the excellent photocatalytic effect for dye degradation should be attributed to the synergistic effects between photo-decomposition of the supported TiO₂ and adsorptivity of the porous carbons.

Keywords: C/TiO₂, Surface area, SEM, XRD, EDX, Photocatalyst

1. Introduction

Titanium oxide has been widely studied as a promising material for an environmental protection and architectural engineering approach for the past few decades because of its excellent photocatalytic activity. A number of studies have shown their unique performance in a photodegradation of most organic toxic compounds in a wastewater.¹,² According to former studies for the carbon sources, the carbonization of an unlinked resorcinol resin with titanium tetrabutoxide,³ immersion of activated carbon in a TiO₂ sol,⁴ and mechanical grinding of activated carbon with TiO₂⁵ have been reported for the preparation of carbon/TiO₂ composites. More recently, the combination of carbonaceous materials with photocatalysts has been of interest. It is important to quantify the impact that irradiations of the carbon/TiO₂ have a photocatalytic activity. The roles of carbon at the carbon/anatase-type titanium dioxide complex were found to have many advantages such as high photosensitivity, high photocatalytic activity and high adsorptivity.¹,⁶-⁸ According to an early study,⁹ it is suggested that the contaminant molecules in carbon-coated TiO₂ have to be adsorbed into the carbon layer that covers the TiO₂ particle, diffuse through the carbon layer to reach the surface of the TiO₂ photocatalyst and then be decomposed under UV irradiation. Composite product of carbon and TiO₂ photocatalysts may offer 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 some reasons; adsorption and release capability for the pollutants onto the surface of TiO₂, increase of charge transference between porous carbon and TiO₂ by acidification of surface hydroxyl groups and adsorption of intermediates produced during degradation. 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/TiO₂ complex particles have on an adsorption ability to the catalyst particles, to transfer the adsorbates to the surface of the TiO₂.

In this study, we have prepared hybrid complexes of carbon and titanium oxide for synergistic effects by the combined function of adsorptivity and photoactivity. The preparation methods of hybrid C/TiO₂ complexes used the penetration of titanium n-butoxide (TNB) solution with porous activated carbon and its fibers. The C/TiO₂ complexes prepared were characterized by their 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 catalysts studied was evaluated by the photodegradation of methylene blue (MB).

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2. Experiment

2.1. Materials

A granular type activated carbon used in this study 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. And, 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 at a 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 damage to the ACF surface. The oxidation was carried out at the boiling temperature for 1 hr. The oxidized ACFs were washed and dried at 323 K for 24 hr. The powder mixtures in the solution before the preparation of C/TiO₂ complexes were heated at 333 K for 6 hr. After a heating, the solvent in the mixtures was vaporized at 353 K for 1 hr. We prepared activated carbon and activated carbon fiber slurry solutions with pristine concentrations of 30 mL of titanium n-butoxide (TNB, C₁₆H₃₆O₄Ti, Acros Organics, USA) for the preparation of C/TiO₂ complexes. For the preparation, 3 g of powdered activated carbon and activated carbon fiber were mixed in to 30 mL of TNB aqueous solutions and stirred for 5 hr at 333 K. The agglomerates of C/TiO₂ complexes prepared were heated at 973 K for 1 hr and then crushed in an auto miller. The nomenclatures and preparation conditions of samples are listed in Table 1.

2.2. Characterization

For the physical parameter measurements, nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics, USA) at 77 K. X-ray diffraction patterns were taken using an X-ray diffractometer (Shimadzu XD-D1, Japan) with Cu Kα radiation. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of C/TiO₂ complexes prepared through the TNB method. For the elemental analysis of the C/TiO₂ complexes, energy dispersive X-ray analysis (EDX) was also used. As one of the analysis of photocatalytic activity, UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize the catalytic efficiency C/TiO₂ complex photocatalysts. Characterization of methylene blue (C₁₆H₁₈N₃S, MB) in water was determined by the following procedure. A C/TiO₂ 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 450-800 nm wavelength of MB measured by UV/VIS spectrophotometer.

2.3. Photocatalytic Effect

In order to reveal the photocatalytic effect of the C/TiO₂ 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 a 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.

3. Results and Discussion

3.1. Physical Analysis and Surface Morphology

Table 2 is compiled for the surface properties of the C/TiO₂ complexes prepared from TNB methods. By using ceramic substrate, carbon coating was experimentally exposed so that the carbon formed on most ceramic surface from carbon precursors was highly microporous. The BET surface area for C/TiO₂ named as AT33 prepared at 973 K had a low value with a dependency on the activated carbon precursor. According to a former study, it was found that the original pristine TiO₂ produced a very small surface area (about 2 m²/g). The result of the table for the AFT33 demonstrates that the sample reveals a slight increase in the BET surface area as complex samples by addition of activated carbon fiber. However, almost all the surface textural parameters for the complexes were considerably more decrease than that of precursor porous carbons. This could be attributed to the formation of TiO₂ on the carbon surface and the blocking of micropores during TNB treatment. It was considered that the formation of TiO₂ and TNB on the carbon surface could be blocked to pore in activated carbon or activated carbon fiber, but surface properties of porous carbons were transformed by heat treatment. It is outstanding that variations of surface parameters among complexes are related to removal efficiency of dye and other pollutants by adsorptivity. Because the TiO₂ only presented some macropores and did not present either mesopores or micropores, they had a low surface area value. The result of the table for the AAFT55 demonstrates that the sample reveals a slight increase in the BET surface area by a reaction with activated carbon fiber pre-treated with acid than that of AFT33. However, almost all the surface textural parameters for the samples were

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mixing ratios</th>
<th>Nomenclatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon + TNB</td>
<td>AC 3g + TNB 30 mL</td>
<td>AT33</td>
</tr>
<tr>
<td>Activated carbon fiber + TNB</td>
<td>ACF 3g + TNB 30 mL</td>
<td>AFT33</td>
</tr>
<tr>
<td>Acid treated activated carbon fiber + TNB</td>
<td>ACF 3g pre-treated with 0.5 M HNO₃ + TNB 30 mL</td>
<td>AAFT55</td>
</tr>
</tbody>
</table>
Table 2. Surface textural properties of pristine materials and samples prepared as different types of C/TiO$_2$ complexes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameter</th>
<th>SBET (m$^2$/g)</th>
<th>Micropore volume (cm$^3$/g)</th>
<th>Internal surface area (m$^2$/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received TiO$_2$</td>
<td></td>
<td>125.0</td>
<td>-</td>
<td>87</td>
<td>-</td>
</tr>
<tr>
<td>As-received activated carbon</td>
<td></td>
<td>1829</td>
<td>0.412</td>
<td>1597</td>
<td>17.28</td>
</tr>
<tr>
<td>As-received activated carbon fiber</td>
<td></td>
<td>1989</td>
<td>0.443</td>
<td>1645</td>
<td>17.56</td>
</tr>
<tr>
<td>AT33</td>
<td></td>
<td>723</td>
<td>0.286</td>
<td>645</td>
<td>15.27</td>
</tr>
<tr>
<td>AFT33</td>
<td></td>
<td>785</td>
<td>0.331</td>
<td>668</td>
<td>14.95</td>
</tr>
<tr>
<td>AAFT55</td>
<td></td>
<td>873</td>
<td>0.324</td>
<td>682</td>
<td>15.36</td>
</tr>
</tbody>
</table>

Fig. 1. SEM micrographs of C/TiO$_2$ complexes; (a) AT33, (b) AFT33 and (c) AAFT55.
After the heat treatment at 973 K for 1 hr for all of samples, the main crystalline phase was presented as an anatase structure by transformation of TNB.

For the elemental analysis of C/TiO$_2$ complexes prepared as a function of carbon sources, these samples were analyzed by EDX. The EDX spectra of C/TiO$_2$ complexes is shown in Fig. 3. Most of these samples were richer in carbon and major Ti metal than any other elements. These spectra showed the presence of C, O and strong Ti peaks with some kind of metallic peak as an impurity. These results were observed for each sample and showed the spectra corresponding to complexes rich in C atom as major element. In the case of most of the samples, carbon and Ti were present as major elements in the C/TiO$_2$ complexes. The results of EDX elemental analysis of C/TiO$_2$ complexes are listed in Table 3.

### Table 3. EDX elemental microanalysis of C/TiO$_2$ complexes prepared as different types

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT33</td>
<td>50.8</td>
<td>24.6</td>
<td>23.5</td>
<td>1.12</td>
</tr>
<tr>
<td>AFT33</td>
<td>58.7</td>
<td>21.7</td>
<td>19.5</td>
<td>0.11</td>
</tr>
<tr>
<td>AAFT55</td>
<td>28.7</td>
<td>29.4</td>
<td>41.8</td>
<td>0.13</td>
</tr>
</tbody>
</table>

#### 3.3. Comparative Analysis by Photocatalytic Activity

The results for a comparative analysis of dye decomposition could be obtained by UV/VIS spectroscopy. The UV/VIS absorbance spectra of initial MB concentration at 5.0$\times$10$^{-5}$ mol/L against the C/TiO$_2$ complexes prepared by TNB methods are shown in Fig. 4. The maxima values of absorbance for all the samples slowly decreased with an increase of UV irradiation time. This indicates that the transparency of the MB concentration was highly increase by a photocatalytic degradation effect of C/TiO$_2$ complexes. Fig. 5 presents the degree of dye degradation with change in MB concentration under UV light irradiation in the solution after dispersion of C/TiO$_2$ photocatalysts. The dye degradation with C/TiO$_2$ photocatalysts was carried out to observe the photo-decomposition effect for the MB solution. It was observed that the dye in the solution was quite unstable with variation of time when it was irradiated under UV light with C/TiO$_2$ photocatalysts, suggesting that the disappearance of dye was caused by a UV irradiation. The changes were plotted on the relative concentration (c/co) of MB in the aqueous solution with UV irradiation time for the C/TiO$_2$ complexes. The slopes showed the plot depends on the irradiation time, as reported for similar modified TiO$_2$ samples. Because the porous carbon in C/TiO$_2$ complexes had a large adsorptivity, it is believed that the decrease of dye concentration in the aqueous solution could occur as a synergic phenomena such as adsorption by porous carbon and photo-decomposition by TiO$_2$ formed on the carbon surfaces. The synergic degradation mechanism is shown in Fig. 6. The two physical effects have been ascribed the enhanced adsorption of the pollutants on activated carbon followed by a transfer through an interphase to titania. The photocatalytic activity in the C/TiO$_2$ complexes could be attributed to the homogeneous distribution between titania complexes and porosity of the external surface. By the former study, MB adsorbed on the carbon particles can eventually be decomposed by the TiO$_2$ particles in solution. This suggests that the TiO$_2$ formed on the surface of activated carbon can retain its photocatalytic reactivity. In case of AAFT55, the surface oxidation of activated carbon fiber by acid treatment could 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 could be determined by means of indirect determination, such as measurements of the catalytic activity for the decomposition of pollutants. From the dye removal results measured periodically over 60 min, the increase in the porosity like surface area resulted in a significant degradation effect with decrease of c/co of MB solution. From the results between c/co of MB and UV irradiation time, it was observed that dye removal efficiency in the composites was better than that of pristine TiO$_2$. For all the C/TiO$_2$ complexes prepared by TNB methods, slope...
relationship between $c/c_0$ of MB and UV irradiation time was observed at $5.0 \times 10^{-5}$ mol/L of MB concentration. We therefore can conclude that the effect of dye degradation should be attributed to both effects between photo-decomposition of the supported TiO$_2$ and adsorptivity of the porous carbons.

4. Conclusion

In this study, we have prepared C/TiO$_2$ complexes photocatalysts with TNB methods as a function of various carbon precursors. The photocatalysts were investigated for their surface textural properties and SEM morphology, structural crystallinity and elemental identification between porous carbons and TiO$_2$, and dye decomposition performance. The result of the textural surface properties revealed an increase in the porosity, like surface area, which resulted in a significant degradation effect. The SEM morphologies revealed the surface structure on the C/TiO$_2$ complexes. In the XRD patterns for all C/TiO$_2$ complexes, the diffraction peaks showed the formation of anatase crystallites. The EDX spectra showed the presence of C, O and strong Ti peaks with some kinds of metallic peaks as impurity. Finally, the good photocatalytic activity of the C/TiO$_2$ complexes between $c/c_0$ for MB and UV irradiation time could be attributed to the synergetic effects between photocatalysis of the supported TiO$_2$ and adsorptivity of porous carbons.

References

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