Degradation of Phenol under Visible Light Irradiation Using TiO_2 with Fe^{III} and Easy Sedimentation of TiO_2 Particles

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The combined photocatalytic system (P25 TiO_2 + $Fe(ClO_4)_3$) was visible light active, and the phenol degradation rate was higher than the sum of the rates for the separately used single photocatalyst. The reason is discussed based on the catalytic cycle of Fe^{III}/Fe^{II}. The suspended TiO_2 particles were easily sedimented by neutralizing the suspension.

$[Fe(H_2O)_6]^{3+}$ forms pH-dependent hydrolytic aquacomplexes, such as $[Fe(OH)(H_2O)_5]^{2+}$, $[Fe(OH)_2(H_2O)_4]^{+}$, $[Fe(OH)_3(H_2O)_3]^0$, and $[Fe_2(OH)_2]^{4+}$ (dimer).[1] For simplicity, hereafter, coordinated water molecules are abbreviated. $Fe(OH)^{2+}$, which is a dominant species in an acidic solution (pH 2.5–5), is known to act as a photocatalyst, because it generates OH radical under UV and UV–vis light irradiations.[1,2] The combined use of TiO_2 with Fe^{III} (combined system) has been shown to enhance the degradation of water pollutants under 365 nm[2,3] and solar light irradiations,[4] and the photocatalytic cycle Fe^{III}/Fe^{II} has been proposed.[2] In the acidic solution of $Fe(ClO_4)_3$, the concentration of highly photoactive $Fe(OH)^{2+}$ ($\lambda_{max} = 295$ nm) gradually decreases with aging, and it converts into a less photoactive soluble dimer and oligomers. In addition, the absorption edge of $Fe(OH)^{2+}$ red-shifts from 400 to 600 nm.[5] Therefore, visible light activity by the combined system is expected. On the other hand, it has been stated that in the $FeCl_3/TiO_2$ photocatalytic system, coagulation by $FeCl_3$ is an effective method for the removal of TiO_2.[3] In this study, we examined the visible light activity of the combined system for phenol degradation, the time dependence of related species, and the separation of TiO_2 by coagulation after degradation.

P25 TiO_2 (15–40 nm, 80% anatase + 20% rutile-type crystal structure, bandgap = 410 nm,[6] Nippon Aerosil Co.) and anatase-type ST-01 TiO_2 (7 nm, Ishihara Sangyo Co.) were used. $Fe(ClO_4)_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, and $Fe_2(SO_4)_3 \cdot nH_2O$ were the iron compounds used. The photoirradiation was performed in a 100 mL photoreactor, which was set in a WACOM HX-500Q irradiator equipped with an ultrahigh-pressure Hg lamp (500 W),[7] and visible light (405 nm + 436 nm) was selected on the basis of a previous method.[7] All incident light was absorbed by the TiO_2-suspended Fe^{III} solution, and it was estimated to be 7.95×10^{15} photons $mL^{-1}\,s^{-1}$, using a potassium tris(oxalato)ferrate(III) actinometer. When using the iron salts as a photocatalyst, the salts (0.030 mmol) were separately added to a 100 mL phenol solution (20 µM), and the acidic solutions (pH 3.5) were then immediately irradiated with polychromatic visible light while stirring. The concentration of $Fe_2(SO_4)_3$ was determined by using ICP method. When using the combined photocatalytic system, 0.050 g of P25 TiO_2 and ST-01 TiO_2 were separately added into a 100 mL phenol solution (20 µM), and the suspensions were stirred for 30 min to reach adsorption equilibrium. After addition of the iron salts (0.030 mmol) to the suspension, irradiation was immediately started. The concentration of phenol was periodically measured by HPLC according to a previous method.[8] The concentrations of $Fe(OH)^{2+}$ and Fe^{II} were determined by complexometry using 8-hydroxyquinoline-5-sulfonic acid (HQSA)[9] and 1,10-phenanthroline,[2] respectively. The concentration of •OH was monitored by following the appearance of phenol (HPLC) from the •OH mediated oxidation of added benzene (reaction yield: 70%).[10]

Figure 1 shows the phenol degradation by TiO_2 (P25 and ST-01), $Fe(ClO_4)_3$, and TiO_2 with three Fe^{III} salts under visible light irradiation. An Fe^{III} salt concentration of 0.3 mM has been reported to be optimum for the degradation of water pollutants.[2,11] The addition effect of the Fe salts to TiO_2 were as follows: $Fe(ClO_4)_3$ (P25) > $FeCl_3$ > $Fe_2(SO_4)_3$ > only p25 TiO_2 > $Fe(ClO_4)_3$ (ST-01) > only $Fe(ClO_4)_3$ > only ST-01 > photolysis. The phenol degradation rate increased when the Fe^{III} salts were added to the P25 TiO_2 suspension. ST-01 TiO_2 (anatase) was ineffective in the combined system. When $Fe(ClO_4)_3$ was added to P25 TiO_2, the apparent first-order rate constant was 6.5 times greater than the sum of single systems: k_{obs} (min^{-1}) 0.0448 for TiO_2 + $Fe(ClO_4)_3$, 0.0046 for TiO_2, and 0.0023 for $Fe(ClO_4)_3$. The synergetic effect is greater than that when manuron is degraded by the combination of TiO_2

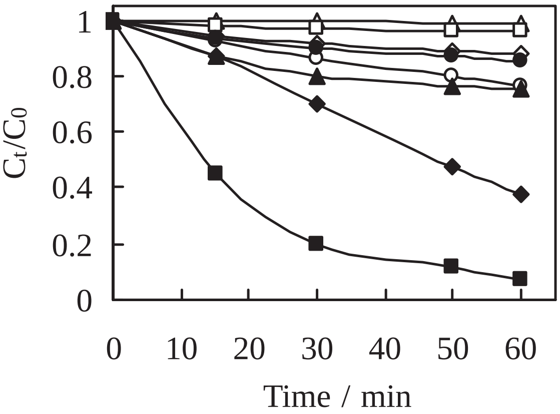

Fig. 1. Degradation of phenol by TiO_2, $Fe(ClO_4)_3$, and TiO_2 with three Fe^{III} salts under visible light irradiation. △: direct photolysis, □: ST-01 TiO_2, ◇: $Fe(ClO_4)_3$, ○: P25 TiO_2, ▲: P25 TiO_2 + $Fe_2(SO_4)_3$, ◆: P25 TiO_2 + $FeCl_3$, ■: P25 TiO_2 + $Fe(ClO_4)_3$, ●: ST-01 TiO_2 + $Fe(ClO_4)_3$.

Published on the web May 14, 2007; doi:10.1246/bcsj.80.1017

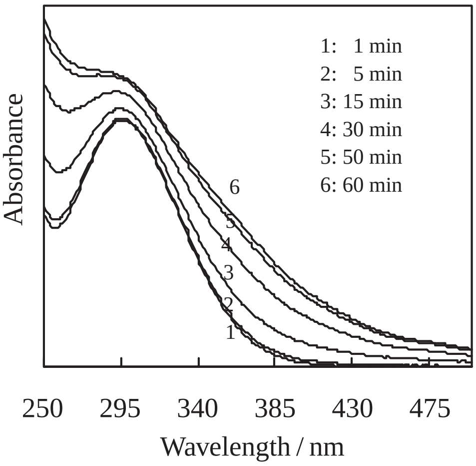

Fig. 2. UV–visible absorption spectra of 0.3 mM $Fe(ClO_4)_3$ aged from 1 to 60 min at pH 3.5 under dark.

and $Fe(ClO_4)_3$ under UV light irradiation.[11]

To elucidate why the combined system is visible light active, we measured the UV–visible absorption spectra of 0.3 mM $Fe(ClO_4)_3$ aged from 1 to 60 min in the dark. The results are shown in Fig. 2. $Fe(OH)^{2+}$ showed an absorption maximum at 295 nm, and an absorbing tail extended up to 410 nm. The aging decreased the net absorbance at 295 nm and shifted the absorption tail to more than 500 nm with increasing absorbance. These results can be explained by the conversion of the most photoactive $Fe(OH)^{2+}$ into the less photoactive dimer and oligomers.[5] Although the photoactivity decreased, the red shift and the increasing absorbance would induce the visible light activity in the combined system.

Since the time dependence of $Fe(OH)^{2+}$ and Fe^{II} ions in the combined system under irradiation has not yet been reported, the results were compared to that of the $Fe(ClO_4)_3$ system. Figure 3 represents the time dependence of the $Fe(OH)^{2+}$ and Fe^{II} ions concentrations for two photocatalytic system under dark and visible light (TiO_2: P25). In the dark, using $Fe(ClO_4)_3$, the concentration of $Fe(OH)^{2+}$ exponentially decreased to 46% at 60 min, because $Fe(OH)^{2+}$ was converted into the dimer and oligomers.[5] Under irradiation with $Fe(ClO_4)_3$, the concentration of $Fe(OH)^{2+}$ decreased with increasing concentrations of Fe^{II} ions and $\bullet OH$ (Fig. 4). However, the slightly higher concentration level of $Fe(OH)^{2+}$ compared to that in the dark can be explained by its regeneration[2] via $Fe^{II} + \bullet OH \rightarrow Fe(OH)^{2+}$. In the dark with TiO_2 and $Fe(ClO_4)_3$, 74% of the $Fe(OH)^{2+}$ was adsorbed on the surface of the TiO_2 after 2 min. When the photoirradiation started, the concentration of $Fe(OH)^{2+}$ gradually increased, while the concentration of Fe^{II} ions increased much faster than for the $Fe(ClO_4)_3$ system, and after 60 min, it reached a value that was 4.5 times higher than without TiO_2. The adsorption of Fe^{III} ions on the surface of TiO_2 is much higher than Fe^{II} ions.[12] Therefore, Fe^{III} would be rapidly reduced to Fe^{II} by photoexcited electrons on the surface of TiO_2, and the reoxidation of Fe^{II} by holes would be reduced due to the rapid desorption of the resultant Fe^{II} ions.

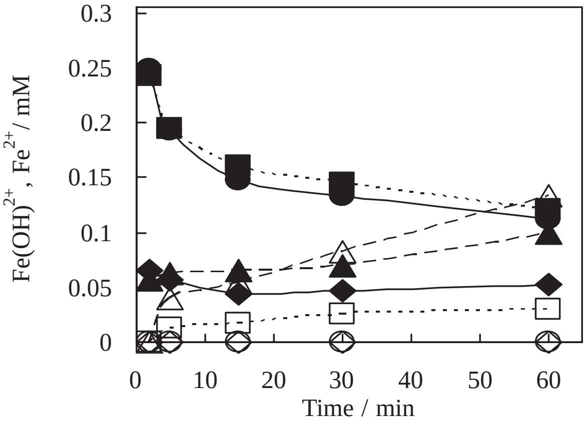

Fig. 3. Time dependence of the concentrations of $Fe(OH)^{2+}$ and Fe^{II} ions for two catalytic systems under dark and visible light irradiations. □: [Fe^{II}], under light with $Fe(ClO_4)_3$; △: [Fe^{II}], under light with TiO_2 and $Fe(ClO_4)_3$; ◇: [Fe^{II}], under dark with TiO_2 and $Fe(ClO_4)_3$; ○: [Fe^{II}], under dark with $Fe(ClO_4)_3$; ■: [$Fe(OH)^{2+}$], under light with $Fe(ClO_4)_3$; ▲: [$Fe(OH)^{2+}$], under light with TiO_2 and $Fe(ClO_4)_3$; ◆: [$Fe(OH)^{2+}$], under dark with TiO_2 and $Fe(ClO_4)_3$; ●: [$Fe(OH)^{2+}$], under dark with $Fe(ClO_4)_3$.

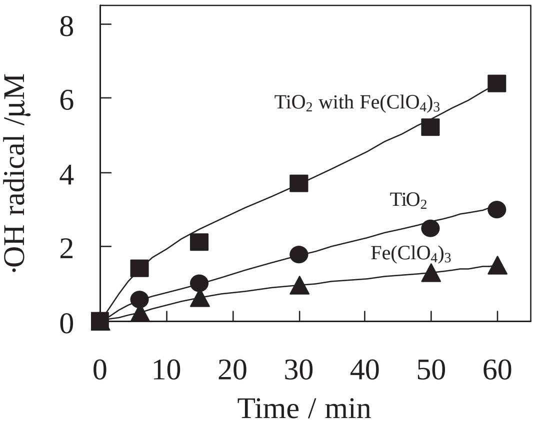

Fig. 4. Comparison of OH radical formation for three photocatalysts under visible light irradiation.

Figure 4 shows a comparison of the $\bullet OH$ formation for the three photocatalysts under visible light irradiation. The time profile of $\bullet OH$ increased as parabolic-type curves, and the rates were as follows: the combined system > P25 TiO_2 > $Fe(ClO_4)_3$. The amount of $\bullet OH$ for the combined system was about 1.5 times greater than the sum for $Fe(ClO_4)_3$ and TiO_2.

Figure 5 shows the time dependence of the $Fe(OH)^{2+}$ concentration produced by the hydrolysis of various iron salts. The $Fe(OH)^{2+}$ concentration was affected by the coordination ability of the counter anions for Fe^{III} ions ($ClO_4^- < Cl^- < SO_4^{2-}$). With weakly coordinating ClO_4^-, $Fe(OH)^{2+}$ remains, while with Cl^- and SO_4^{2-}, $Fe(OH)^{2+}$ and photoinactive $FeCl^{2+}$ or $Fe(SO_4)^+$ coexist.[13] Coordination would determine the initial concentration of $Fe(OH)^{2+}$, of which a decrease by oligomerization was clearly observed when $Fe(ClO_4)_3$ was used. The reactivity (Fig. 1) corresponded to the amount of $Fe(OH)^{2+}$.

Figure 6 shows the effect of the aging time on the degradation of phenol. The degradation decreased with aging, showing that a long aging time induced a concentration decrease in

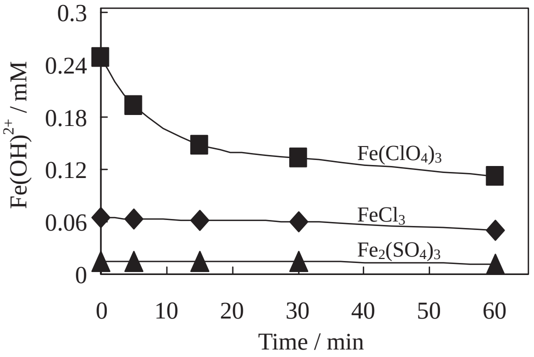

Fig. 5. Time dependence of $Fe(OH)^{2+}$ concentration for three iron salts before light irradiation.

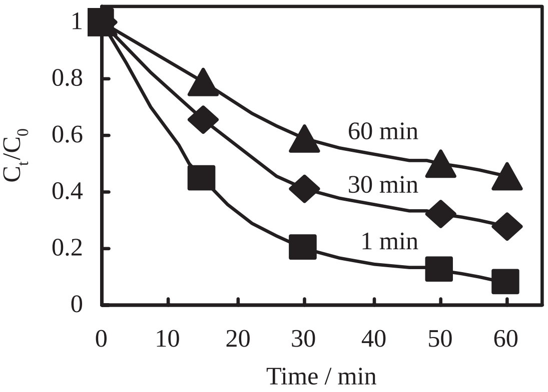

Fig. 6. Effect of the aging time of 0.3 mM $Fe(ClO_4)_3$ with P25 TiO_2 on the degradation of phenol.

•OH with a decrease in the amount of photoactive $Fe(OH)^{2+}$ (Fig. 5). It is necessary to start the reaction quickly when 0.3 mM $Fe(ClO_4)_3$ was added to the TiO_2 suspension.

The synergetic effect of the combined system can be explained as follows. (1) $Fe(OH)^{2+}$ and its dimer and oligomers absorb visible light and form Fe^{II} and •OH. (2) The rutile crystal lattice in P25 TiO_2 absorbs visible light, and excited electrons transfer to the lattice electron-trapping sites of the anatase crystal lattice to enhance the charge separation (h^+ and e^-).[6] (3) The trapping of the e^- by the adsorbed Fe^{III} ions reduces the recombination rate of e^- and h^+, because the redox potential of Fe^{III}/Fe^{II} is 0.77 V (vs SHE) higher than the potential of the anatase TiO_2 conduction band.[11] (4) The resultant Fe^{II} ions are removed from the TiO_2 surface and reoxidized by •OH in the solution. (5) The dimer and oligomer can be reduced by the e^-, and the resultant Fe^{II} ions are reoxidized by •OH.[2] This process continuously affords most photoactive Fe^{III} ions (monomer). (6) The •OH and e^- on P25 TiO_2 is continuously afforded into the Fe^{III}/Fe^{II} redox cycle. (7) The •OH, which increases with time (Fig. 4), degrades phenol.

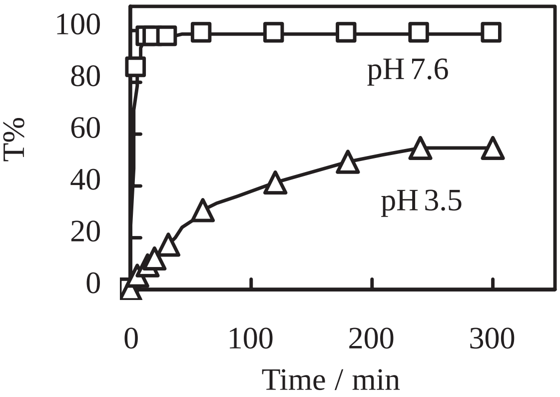

Fig. 7. Effect of pH on the sedimentation of TiO_2 particles after irradiation.

Figure 7 shows the effect of pH on the sedimentation of TiO_2 particles after irradiation for 60 min. Without adjusting the pH to 3.5, a slow coagulation occurred; however, the formation of flocks was not observed due to the electrostatic repulsion of the $TiOH_2^+$ (acid form) species present on the surface of the TiO_2. By neutralizing the acidic solution to pH 7.6 with 0.1 M NaOH, the TiO_2 particles sedimented after about 15 min, and the transmittance (T%) of the supernatant solution was greater than 98.9%. Big and heavy flocks of $Fe(OH)_3$ caused the TiO_2 particles to sediment at a pH greater than 6.9.

In conclusion, the addition of $Fe(ClO_4)_3$ to a P25 TiO_2 suspension significantly enhanced the degradation of phenol under visible light irradiation. Higher concentration of •OH in the combined system than in $Fe(ClO_4)_3$ and TiO_2 systems can be explained by the catalytic cycle of Fe^{III}/Fe^{II}. Neutralization of the solution after irradiation enabled the sedimentation of the TiO_2 particles.

This research was financially supported by a grant-in-aid for Scientific Research (No. 17510063) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1 B. C. Faust, J. Hoigne, *Atmos. Environ.* **1990**, *24*, 79.

2 H. Měšt'ánková, G. Mailhot, J. Jirkovský, J. Krýsa, M. Bolte, *Appl. Catal., B* **2005**, *57*, 257.

3 W. Baran, A. Makowski, W. Wardas, *Chemosphere* **2005**, *59*, 853.

4 C. Domínguez, J. García, M. A. Pedraz, A. Torres, M. A. Galán, *Catal. Today* **1998**, *40*, 85.

5 H. Krysova, J. Jirkovsky, J. Krysa, G. Mailhot, M. Bolte, *Appl. Catal., B* **2003**, *40*, 1.

6 D. C. Hurum, A. G. Agrios, S. E. Crist, K. A. Gray, T. Rajh, M. C. Thurnauer, *J. Electron Spectrosc. Relat. Phenom.* **2006**, *150*, 155.

7 K. Hasegawa, T. Kanbara, S. Kagaya, *Denki Kagaku* **1998**, *66*, 625.

8 M. S. Nahar, K. Hasegawa, S. Kagaya, *Chemosphere* **2006**, *65*, 1976.

9 N. Brand, G. Mailhot, M. Bolte, *Environ. Sci. Technol.* **1998**, *32*, 2715.

10 B. C. Faust, J. M. Allen, *Environ. Sci. Technol.* **1993**, *27*, 1221.

11 H. Měšt'ánková, J. Krýsa, J. Jirkovský, G. Mailhot, M. Bolte, *Appl. Catal., B* **2005**, *58*, 185.

12 T. Ohno, D. Haga, K. Fujihara, K. Kaizaki, M. Matsumura, *J. Phys. Chem. B* **1997**, *101*, 6415.

13 L. Garrel, M. Bonetti, L. Tonucci, N. d'Alessandro, M. Bressan, *J. Photochem. Photobiol., A* **2006**, *179*, 193.