Comparative assessment of the efficiency of Fe-doped TiO₂ prepared by two doping methods and photocatalytic degradation of phenol in domestic water suspensions

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Abstract

Fe-doped TiO₂ particles responding to visible light were synthesized by impregnation and calcination method using TiO₂ particle and Ti element, respectively. The optical and the chemical properties were characterized by measuring the X-ray diffraction (XRD) and UV–visible spectroscopy. The onset of absorption shifted to longer wavelengths on doping TiO₂ by the calcination process, which showed a better response as compared to the impregnation method. The photocatalytic reactivity was evaluated by the degradation of phenol with impregnated Fe-doped (0.5% w/w in Fe) and calcined Fe-doped (FeₓTi₁₋ₓO₂, x = 0.005 (Fe/Ti molar ratio)) TiO₂ separately in distilled and tap water. The characterization results have confirmed the advanced possibility of correlation between photoactivity and the special property of sulfur-containing calcined Fe-doped TiO₂. In case of the coagulation of the undoped A-I and the Fe-doped B-I, the photoactivity showed a decrease due to the presence of natural electrolytes and due to the high pH of tap water, whereas in the case of the coagulation of calcined Fe-doped TiO₂ prepared from sulfides (FeₓTiS₂), the photoactivity showed an increase. In this study, highest catalytic activity was found to be strongly dependent both on catalyst structure and on the type of water used.

Keywords: Tap water; TiO₂; Phenol; Photodegradation; Dopant; Calcination; Sulfidation; pH; Visible; Impregnation

1. Introduction

Semiconductor-mediated photocatalytic oxidation is widely used to destroy water pollutants. Among the semiconductors that are being studied, TiO₂ is one of the most efficient photocatalyst. However, it is generally reported that method of preparation and structural parameters strongly affect the photocatalytic activity of TiO₂ for pollutant degradation [1]. In addition, the effect of dopant has a primary role in extending the light absorption and conversion capacities of TiO₂ to the visible light. A wide range of metal ions have been used to prepare the chemically metal-doped TiO₂ [2–8], the physically metal-implanted TiO₂ [9–11], and the TiO₂-based binary oxide [4]. Their effects on the properties of the doped samples have been reported. Some research groups attempted to modify TiO₂ such that it showed response to visible wavelength through the use of oxygen-vacant TiO₂ [12], nonmetal-doped TiO₂ [13,14], and metal–nonmetal co-doped TiO₂ [15] particles that have significant photocatalytic activity.

Although many studies have been reported on the photocatalytic degradation of pollutants in distilled water suspensions, only few investigations on the photocatalytic activity of catalysts have been performed in domestic [16] and natural water [17] sources. The very common pollutant properties of industrial effluents are attributed to phenolic compounds. Degradation of such organic pollutants by TiO₂ holds promise for the purification and treatment of both drinking and industrial wastewater [18]. The effect of environmental electrolytes and natural pH of the tap and well water in Toyama city, Japan, has been investigated for promoting the separation of P25 TiO₂ after photoirradiation [16]. It has been found that it is difficult to retard coagulation of P25 TiO₂ at the time of photoirradiation.

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2. Experimental

2.1. Materials

Degussa P-25 TiO₂ powder (obtained from Nippon Aerosil Co., Japan) and iron nitrate (from Kanto Chem Co. Ltd., Japan) were used as the starting materials for the impregnation method. The starting chemicals of the calcination method were titanium (powder), sulfur (powder), and iron (powder), which were purchased from Wako Pure Chemical Industries Ltd., Japan. Phenol and acetonitrile (HPLC grade) were obtained from Wako Pure Chemical Industries Ltd., and was used as received.

2.2. Preparation of doped catalyst

Two methods have been used to prepare the Fe-doped and undoped TiO₂ catalyst, respectively.

2.2.1. Impregnation method

In this method [19], samples A-I and B-I prepared from the mixture of P25 with Fe(NO₃)₃ (Fe wt % = 0, 0.5%), were stirred for 48 h and heated at 120 °C for 24 h to evaporate the liquid phase and calcined in air at 500 °C for 24 h.

2.2.2. Calcination method

In this method, the powdered forms of elements (Ti, S, and Fe) were subjected to sulfidation at 800 °C for 96 h in an evacuated quartz tube. The sulfide sample (FeₓTiS₂) was calcined at 550 °C for 2 h to produce calcined FeₓTi₁₋ₓO₂ samples [20], and the undoped and optimum Fe-doped TiO₂ samples with x = 0 and 0.005 (x = Fe/Ti ratio) were denoted as A-C and B-C, respectively. The diameter of a unit particle of the Fe-doped TiO₂ was measured using an optical microscope.

2.3. Analysis

2.3.1. The X-ray photoelectron spectra (XPS)

The XPS of the Fe-doped TiO₂ powder obtained were performed using a Shimadzu ESCA-3400 photoelectron spectrometer with an MgKα source (1253.6 eV). The shift in the binding energy due to the relative surface charging was corrected using the carbon-1s level at 284.80 eV as the internal standard.

2.3.2. X-ray diffraction spectroscopy

XRD scans were recorded using CuKα radiation (40 kV) in a Rigaku RINT Ultima+ at the scan rate of 3° min⁻¹.

2.3.3. UV–visible spectroscopy

The UV–visible diffuse reflectance spectra were measured in the wavelength range from 250 to 650 nm using a Shimadzu UV–vis spectrophotometer (UV 3100 PC, MPC-3100) with BaSO₄ as the reference.

2.3.4. HPLC system

The degradation of phenol was performed using a JASCO HPLC system equipped with a PU-980 pump, a 970 UV–vis detector (λ = 269 nm), and a Mightysil RP-18 column. A mixture of CH₃CN: H₂O = 40:60 was used as the mobile phase.

2.3.5. UV spectrophotometer

The transmittance of the transparent upper layer of irradiated mixture was measured at 400 nm using a Shimadzu UV-1600 spectrophotometer.

2.4. Tap water

The compositions of environmental electrolytes and natural pH of the tap and well water in Toyama city, Japan, were recorded as follows: tap water (in mg L⁻¹) [Na⁺] = 1.9, [K⁺] = 0.5, [Ca²⁺] = 7.8, [Mg²⁺] = 1.0, [Cl⁻] = 3.3, [SO₂⁻₃] = 9.0, [HCO₃⁻] = 18.9, pH 7.2–7.23; well water (in mg L⁻¹) [Na⁺] = 4.9, [K⁺] = 0.7, [Ca²⁺] = 11.9, [Mg²⁺] = 2.0, [Cl⁻] = 4.6, [SO₂⁻₃] = 7.9, [HCO₃⁻] = 39.4, pH 7.18–7.21. [16].

2.5. Photoreactor

The light source was a WACOM HX-500Q photoreactor equipped with an ultrahigh-pressure Hg lamp (500 W) (shown in Fig. 1) [21]. The collimated beam of 50 mm diameter that passed through a 12.0-mm pinhole was irradiated onto a cylindrical Pyrex reaction cell (100 mL: 50 mm i.d. × 51 mm length) with a water jacket. The inner wall of the jacket was plated with silver to prevent light-scattering losses from the reaction cell. Pyrex (λ > 290 nm) and Toshiba UV-35 (λ > 350 nm) cutoff filters and Toshiba UV-D36A band-pass filter (300 nm < λ < 380 nm) were used for 365-nm light source. For light sources of 405 and 436 nm, a cutoff filter (0.25 M NaNO₃ + 0.10 M NaNO₂, λ > 385 nm) and a Corning 7–59 band-pass filter (290 nm < λ < 520 nm) were used. Potassium tris(oxalato)-ferrate(III) actinometer, Fe-doped TiO₂-, and P25 TiO₂-suspended solutions were added to the cells, and the quantities of incident light (I₀), absorbed light, and transmitted light were estimated by measuring the photons absorbed in the actinometer, which were set just behind the three cells. I₀ (photons mL⁻¹ s⁻¹) was estimated to be 7.95 × 10¹⁵ for the polychromatic visible light.
\( \lambda = 405 \text{ nm} + 436 \text{ nm} \) and \( 2.14 \times 10^{15} \) for the UV light \( \lambda = 365 \text{ nm} \).

### 2.6. Photoirradiation

First, the natural pH (7.18–7.21) of the tap water was adjusted to 3.8 by adding sulfuric acid in case of the impregnated A-I and B-I catalysts. Samples A-C and B-C reduced the pH value of the tap water spontaneously and prevented coagulation without any addition of acid solution to the reaction mixture. TiO\(_2\) is found to be most active at pH 3.5, and it has been reported in the previous study by the authors [20] that the calcined Fe-doped TiO\(_2\) powder containing S\(^{6+}\) in anatase phase reduced the pH of the suspension to 3.8 and showed the highest activity. Therefore, to avoid the effect of \([\text{SO}_2\text{O}_4^{-}] \) and Na\(^+\), the pH values of the calcined sample suspensions were not adjusted by adding H\(_2\)SO\(_4\) or NaOH solution. The TiO\(_2\) catalyst (0.050 g) was added to a 100 mL phenol solution (1.88 mg/L) in the reaction cell and the suspension was magnetically stirred in dark for 30 min to reach adsorption equilibrium. Irradiated solution (2 mL) was withdrawn from the reactor after certain intervals and was filtered through a syringe equipped with a disposable filter having a pore size of 0.2 \(\mu\)m. The concentration of phenol in the filtrate was measured by HPLC with an UV–visible detector at 269 nm using an ODS column and a mobile phase (CH\(_3\)CN 40% + H\(_2\)O 60%).

### 3. Results and discussion

The diameter of a unit particle for B–C (Fig. 2) was 1.9–2.0 \(\mu\)m, which was 80 times larger than that of P25 (TiO\(_2\))

#### 3.1. UV–visible absorption spectra

The diffuse reflectance spectra for the Fe-doped TiO\(_2\) are shown in Fig. 3. The undoped TiO\(_2\) absorbed light with wavelength shorter than 400 nm (Fig. 3), as the TiO\(_2\) anatase phase has band gap of about 3.2 eV. If two undoped samples A-I and A-C were compared, the absorbed light for A-C was found to correspond to the longer wavelength compared with A-I, with the higher absorption being attributed to the 2.4% sulfur. A higher absorption was observed for Fe-doped TiO\(_2\) obtained from Ti element than that obtained from TiO\(_2\) particle. Color of pure anatase (A-C) was off-white, that of Rutile–anatase mixture (A-I) was white, and that of Fe-doped TiO\(_2\) was yellow for B-C sample and orange to yellow for B-I sample. Therefore, the Fe-doped TiO\(_2\) exhibited intensive visible
light absorption compared with the pure component for the charge-transfer transition between the d-electrons of the doped Fe$^{3+}$ and the TiO$_2$ conduction band [6,22]. The increase in the visible absorption of the UV–visible absorption spectra depended on the method of preparation and on the content of Fe dopant and was of the following order, B-C > B-I > A-C > A-I.

3.2. X-ray diffraction spectra

The XRD of impregnation-derived catalysts showed peaks due to rutile and anatase phases. No XRD peak due to rutile phase was observed for calcination-derived TiO$_2$. Fig. 4 shows the XRD spectra for Fe$^{3+}$-doped TiO$_2$. The polycrystalline anatase structure was confirmed by (1 0 1), (1 0 3), (0 0 4), (1 1 2), and (2 0 0) for all impregnated (A-I, B-I) as well as calcined (A-C, B-C) samples, and the presence of the rutile phase was confirmed by 1 1 0, 1 0 1, 1 1 1, and 2 1 0 diffraction peaks only for impregnated samples (A-I and B-I). Table 1 shows the relative intensities of the main anatase peaks ($d_{hkl}$ 1 0 1) of A-I and A-C that have been reduced by doping; therefore, the peaks of B-I and B-C corresponded to shorter intensities. The relative rutile ($r_{hkl}$ 1 1 0) peak intensities for samples A-I and B-I were almost same. The full-width at half-maximum (FWHM) values have been increased by dopant ions in TiO$_2$ crystal; the FWHM values of Fe-doped B-C particles were reported to be greater than those of doped B-I particles.

The average crystallite size, \(d\), was estimated from the FWHM of the (1 0 1) peak using the Scherrer Eq. (1) [23],

\[
d = \frac{0.94\lambda}{\beta \cos \theta},
\]

(1)

\(\beta\) is the FWHM (radian), \(\lambda = 1.54056\) Å.

The crystallite size calculated for anatase (1 0 1) peak turned out to be 36 nm for A-C, 28 nm for B-C, 35 nm for A-I, and 30 nm for B-I. This result shows that in the impregnation method, Fe influenced the crystalline growth of the anatase TiO$_2$. As revealed by Fig. 4, the Fe-doped specimen presented less anatase than the bare TiO$_2$ did [24].

3.3. XPS study

Fig. 5 shows the XPS Ti (2p$_{3/2}$) peak position of the pure anatase-type TiO$_2$ (A-C) was 459.8 eV and that of Ti (2p$_{1/2}$) to 465.75 [25]. For metallic Ti$^0$, these two peaks would appear to 455 and 459 eV [26]. The peak shifts in Ti (2p$_{3/2}$) and Ti (2p$_{1/2}$) caused by the presence of tetravalent Ti$^{4+}$ is also consistent with TiO$_2$ formation. The atomic concentrations of the element in the doped samples B-C were 55.45% O, 16.24% Ti, and 2.4% S. The peak of S 2p$_{3/2}$ due to S$^{6+}$ appeared at the peak position of 168.8 eV.

![Fig. 4. X-ray diffraction patterns of undoped and Fe-doped TiO$_2$. A-I: Fe = 0; B-I: Fe wt% = 0.5%; A-C: Fe = 0; B-C: Fe = 0.005.](image)

![Fig. 5. S 2p XPS of Fe-doped TiO$_2$ (sample B-C) powder obtained after calcinations at 550 °C.](image)

| Types of catalyst (Fe content = x) | Relative intensity for Anatase ($d_{hkl}$ 1 0 1), | Rutile ($r_{hkl}$ 1 1 0) | FWHM $\beta$(rad) ($d_{hkl}$ 1 0 1) | Crystallite size (nm) |
|---------------------------------|---------------------------------|----------------|-------------------------------|-----------------|
| A-I (x = 0)                    | $d_{1805}$                      |                | 0.084294                      | 35              |
| B-I (x = 0.5% w/w in Fe)       | $d_{1625}$                      |                | 0.085341                      | 30              |
| A-C (x = 0)                    | $d_{1725}$                      | $r_0$          | 0.084102                      | 36              |
| B-C (x = 0.005 Fe/Ti molar ratio) | $d_{405}$                      | $r_0$          | 0.086563                      | 28              |
3.4. Photocatalytic irradiation of phenol by visible light for tap water and distilled water using doped and undoped TiO₂ particles

Visible irradiation of phenol was performed using calcined and impregnated catalyst without changing the natural pH of tap water and distilled water suspensions. The degradation rate increases in the order: B-C > B-I > A-I > A-C for tap and distilled water (Fig. 6), whereas the visible light absorption increases in the order: B-C > B-I > A-C > A-I (Fig. 3). Choi et al. [22] elucidated that the Fe³⁺ dopant in TiO₂ acts as electron and hole trappers to reduce the photo-generated hole–electron recombination rate.

On the basis of the linear relationship shown in Fig. 6, the degradation of phenol follows the first-order kinetics of the concentration of phenol as depicted by

\[ -\ln \left( \frac{C_t}{C_0} \right) = k_{obs} t, \]

where \( k_{obs} \) is the observed rate constant, and \( C_0 \) and \( C_t \) are the concentrations of phenol at \( t = 0 \) and \( t \), respectively.

In case of impregnated catalyst, samples A-I and B-I precipitated due to the natural high pH (7.18–7.21) of tap water, thereby leading to a decrease in the degradation rate. The degradation rate in case of sample B-C increased by decreasing the pH of tap water from 7.2 to 3.8, which is attributed to the presence of SO₂ [20]. But the degradation rate for sample B-C was higher in distilled water as compared to tap water, which is attributed to the effect of ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, [HCO₃⁻]) in tap water. The photocatalysis order is different with B-C in Fig. 6, for its high visible light absorption properties (Fig. 3) and the absence of electrolytes in distilled water.

3.5. Evaluation of UV activity of doped catalyst in tap water obtained by the two doping method

The method that has been used promoted the degradation of phenol by inhibiting the coagulation of the suspended TiO₂ in tap water suspensions. The efficiency of UV photodegradation of phenol as a function of catalyst’s nature is shown in Fig. 7 at the adjusted pH of 3.8. The degradation rate for P25 (TiO₂) was decreased by doping, and this value was about 1.6 times lesser than that of the impregnated Fe-doped sample B-I. At the optimum doping amount of Fe-doped TiO₂ (sample B-C), the rates under UV light were 1.4 times greater than those of A-C (Fe = 0).

In Fig. 7, the dopant acts as an electron trapper in calcined sample B-C and enhances the UV activity better than the undoped sample A-C. Impregnated doped-sample B-I might contain some amorphous type of iron oxide, which may not be detected by XRD (Fig. 3), but it can act as a recombination center [20,22] and decrease the UV activity of the doped sample (B-I) more than the undoped sample (A-I).

Electrolytes coagulate the A-I at pH 6.5, and the degradation rate decreases (Fig. 6), whereas at pH 3.8, the coagulation effect of electrolytes have on A-I particles is little, and TiO₂ remains in suspension and becomes active at pH 3.8, so that the degradation rate is increased.

3.6. Time profiles of the phenol concentration and transmittance of the irradiated tap water at different pH ranges

Fig. 8 shows the correlation between the degradation of phenol at natural pH (7.2) and the adjusted pH (3.8) of tap water with the transmittance of tap water in similar suspensions. The phenol degradation by A-I was 70% (T% 0.004) and 30% (T% 96%) at pH values of 3.8 and 7.2, respectively, for an irradiation time of 180 min. Before adding B-I and A-I in tap water suspensions, the pH was adjusted to 3.8 to retard the coagulation. Sedimentation properties of calcined and impregnated samples are different in tap water system. Calcined Fe-doped TiO₂ (B-C) particles could be readily separated from the suspensions just by settling, which is attributed to their higher specific gravity compared with the undoped TiO₂,
but not by coagulation; therefore, sample B-C remains suspended in reaction mixture. In case of impregnated samples, undoped A-I and doped B-I were coagulated due to the presence of electrolytes in tap water at pH above 6.5.

4. Conclusions

Fe-doped TiO₂ photocatalyst could be prepared from Ti element and TiO₂ (P25) particles by using calcinations and impregnation method, respectively. Calcined samples contain only anatase phase, whereas impregnated samples contain anatase and rutile phases for the starting materials P25 (TiO₂). The effect of the doping methods on the TiO₂ efficiency was investigated by performing the photodegradation of phenol under UV and visible light irradiation. The Fe³⁺ ions caused a higher visible light absorption in calcined samples, whereas in the impregnation method, the same Fe³⁺ cation did very little help in visible light absorption. Fe doping increases the UV and visible light activity for calcined catalyst. However, in the doped samples, the visible activity showed an increase and the UV activity showed a decrease compared with the undoped samples synthesized using the impregnation doping method. From XPS, it can be found that the ratio of Ti:O obtained was not 1:2, which could be associated to the H₂SO₄ (from S⁶⁺ ions) present in the outermost part of the TiO₂ surface. The degradation rate of phenol in tap water suspension was lesser than that in distilled water system. This is attributed to the presence of environmental electrolytes and to the coagulation of TiO₂ catalyst, which could be retarded by decreasing the pH of tap water with the addition of sulfur-containing calcined samples during irradiation.

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