Fe$_2$O$_3$/TiO$_2$ nanocomposite photocatalyst prepared by supercritical fluid combination technique and its application in degradation of acrylic acid

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Abstract. Fe$_2$O$_3$/TiO$_2$ nanocomposite photocatalysts were synthesized by supercritical fluid combination technique, consisting of sol-gel method and supercritical fluid drying. The photocatalytic activity of the samples was evaluated by the degradation of acrylic acid. The results indicated that the Fe$_2$O$_3$/TiO$_2$ nanocomposite catalysts prepared by this novel technique showed significant improvement in catalytic activity compared with pure TiO$_2$ or Fe$_2$O$_3$/TiO$_2$ catalysts prepared by traditional drying. Both infrared and ultraviolet spectrum of Fe$_2$O$_3$/TiO$_2$ nanocomposite photocatalysts shift a little to lower wavelength indicating that the absorption threshold of Fe doped nanocomposite photocatalysts shift into the visible light region. This phenomenon was also attested by the photocatalytic degradation test under visible light.

1. Introduction

While acrylic acid and acrylic esters[1] are playing important roles in chemical industry, much attention is being given to their production because of a huge amount of wastewater released in the production.

Semiconductor photocatalysis appears as an emerging destructive technology leading to the total mineralization of most of organic pollutants[2]. It offers various advantages such as low cost, no secondary pollution, photoreaction occurring at room temperature and atmospheric pressure[3]. Although significant progress has been made on the waste water treatment, photocatalytic degradation of industrial wastewater with acrylic acid remains an untouched area.

Although TiO$_2$ is widely used in photocatalyst due to its good optical and electronic properties, chemical stability and non-toxicity and low cost[4], several factors limit its practical application. The first factor is that TiO$_2$ has a wide band gap of 3.2 eV which can only be excited by high energy UV irradiation with wavelength no longer than 387.5 nm. The second factor is that TiO$_2$ has a high recombination of photogenerated electron/hole pairs[5, 6]. One of these materials that has aroused much research interest is the so-called composite semiconductor photocatalyst. It could extend light absorption to the visible light range[7]. A possibility to achieve this goal is to dope the titanium dioxide with transition metal ions. It has been shown that Fe (III) doping can increase the photocatalytic activity of TiO$_2$[8].

In this paper, the nanocomposite photocatalyst Fe$_2$O$_3$/TiO$_2$ was prepared by supercritical fluid combination technique (SCFCT). Its photocatalytic activity for the degradation of acrylic acid under ultraviolet light and visible light was also assessed. The success of the present study should shed a light on the feasible application of acrylic acid in the waste water treatment.
2. Materials and Methods

2.1. Preparation of Catalyst
Surfactant (0.3v%) was added to 0.3 mol·L⁻¹ TiCl₄, stirring vigorously at room temperature. The pH of the solution was adjusted to 8-9. After aging for 16 h, the sol was filtered and washed until no presence of Cl⁻. The water in the sol was replaced by anhydrous ethanol. The alcogel obtained was transferred into an autoclave and dried under the supercritical condition of ethanol (262 °C, 8.5 MPa) to produce aerogel. After calcination at different temperature for 1 h, pure nano-TiO₂ was obtained.

0.1 mol·L⁻¹ Fe(NO₃)₃ and surfactant (0.3v%) was added to 0.3 mol·L⁻¹ TiCl₄ in sequence, stirring vigorously at room temperature. The following processes were carried out as mentioned in above. Finally, different molar percentage of Fe₂O₃/TiO₂ nanocomposite catalysts was obtained.

The composite alcogel was also dried at room temperature and then calcined at different temperature for 1 h in air atmosphere. Then (0.03mol%) Fe₂O₃/TiO₂ composite catalysts were obtained.

2.2. Characterizations
The UV irradiation of the high pressure mercury lamp was measured with the UV radiometer (Beijing Normal University photo electric company). The content of Fe was determined by atomic absorption spectrophotometer (Z-8000). The surface morphologies and particle size were determined from transmission electron micrographs made with Hitach-800 TEM. X-ray diffraction measurements were performed using a Shimadzu HR6000X (Cu target X tube, voltage 40.0 KV, current 30.0 mA). The IR spectra were recorded with a Shimadzu IRPrestige-21 spectrophotometer. Diffuse UV-Vis spectra were obtained with a UV-2501PC Ultraviolet spectrophotometer. The UV irradiation of the high pressure mercury lamp was measured with the UV radiometer (Beijing Normal University photo electric company).

2.3. Evaluation of Photocatalytic Activity
The photocatalytic activities of the synthesized catalysts were examined using a self-designed photocatalytic reaction apparatus. It consists of double-layered cylindrical quartz flask with an ultraviolet lamp (9 W, wavelength: 254 nm, intensity: 5210 μw·cm⁻²) or a solar lamp (18 W) positioned in the middle. Acrylic acid aqueous solution (300 mL, 300 mg·L⁻¹) with the chemical oxygen demand (COD) value of 400~500 mg·L⁻¹ was used as degradation solution. The concentration of catalyst was 1g·L⁻¹. The air was introduced from the bottom of the reaction solution at the rate of 30 mL·min⁻¹. The temperature was maintained at 25±1 °C. Stirring was kept to make sure that catalyst was dispersed evenly in the reaction solution. A small volume of the reaction solution was obtained periodically. After centrifugation, the absorbance of these solutions was measured at 210 nm by B-UV 752 spectrophotometer. The COD value of the reaction solution was determined by potassium dichromate method. The photocatalytic activities were estimated from the degradation rate of acrylic acid.

3. Results and discussion

3.1. Results of AAS and XRD measurements
The results of AAS showed that the content of Fe in the composite photocatalysts was 0.03%, 0.1% and 0.15% (molar percentage), respectively.

Figure1 shows the XRD patterns of selected samples (0.03mol% Fe₂O₃/TiO₂) prepared by SCFCT with calcination at 500 °C, 600 °C, 700 °C and without calcination. The observed patterns can be attributed to the TiO₂ anatase as unique phase, which has diffraction peaks at d₁=0.35256 nm, d₂=0.18945 nm and d₃=0.23768 nm. No transformation from anatase type to rutile type was observed after heat treatment. It confirms the conclusion that TiO₂ prepared by SCFCT exists only as anatase type crystal, that is the drying and crystallizing could be accomplished in a single step in supercritical
fluid drying process[9]. It also can be found that the crystallinity was enhanced by the calcination temperature. There is no peak corresponding to Fe₂O₃ present in the XRD patterns. This result could be attributed to that there is no independent Fe₂O₃ crystalline phase accumulated on the surface of TiO₂, or Fe₂O₃ disperses uniformly in the bulk of TiO₂ particle as very small clusters.

The size of domain crystallite estimated from Scherrer equation was 8.9 nm (without calcination), 10.9 nm (500 ºC), 15.8 nm (600 ºC) and 27.3 nm (700 ºC). These results indicate that the size of the particles increases with the increase of the calcination temperature.

![XRD pattern of Fe₂O₃/TiO₂ samples with different calcinations temperature.](image)

**Figure 1.** XRD pattern of Fe₂O₃/TiO₂ (0.03mol%) samples with different calcinations temperature.

(a) Fe₂O₃/TiO₂ (SCFCT, without calcinations)
(b) Fe₂O₃/TiO₂ (SCFCT, 500 ºC)
(c) Fe₂O₃/TiO₂ (SCFCT, 600 ºC)
(d) Fe₂O₃/TiO₂ (SCFCT, 700 ºC)

3.2. Results of TEM Measurement

![TEM photographs of Fe₂O₃/TiO₂ particles prepared by different methods.](image)

**Figure 2.** TEM photographs of Fe₂O₃/TiO₂ nanocomposite particles prepared by different methods. The TEM photographs of 0.03mol% Fe₂O₃/TiO₂ nanocomposite particles prepared with different methods are shown in figure 2. For the powders obtained using traditional drying (TD) method, the crystals are in the form of aggregates and the composite particles are observed to be 17-23 nm in size (figure 2a). In contrast, the samples prepared by SCFCT have good dispersity. The particle size determined from the TEM graph is 8-10 nm (figure 2b). After calcination at 600 ºC, the particles size is up to 14-18 nm (figure 2c), as is consistent with the size derived from the Scherrer equation.
3.3. Results of IR and UV-Vis

The IR spectra of Fe₂O₃, TiO₂ and 0.03mol% Fe₂O₃/TiO₂ samples are shown in figure 3. In the spectrum of Fe₂O₃/TiO₂, the intensified absorption at about 480 cm⁻¹ is different from that of TiO₂ and Fe₂O₃, which indicates that the formation of a new chemical bond Fe-O-Ti. Figure 3 also shows that the red-shift takes place in the spectra of Fe₂O₃/TiO₂ in comparison with TiO₂, indicating that the absorption threshold of Fe-doped catalyst shift into the visible light region.

The UV-Vis spectra for TiO₂ and 0.03mol% Fe₂O₃/TiO₂ are shown on the figure 4. From the curves we can see that UV-Vis absorbance of 0.03mol% Fe₂O₃/TiO₂ is shifted to longer wavelength (the red shift) compared with TiO₂. The band gap energy (Eg) of anatase TiO₂ extrapolates the absorption edge onto the energy 3.2 ev (387.5 nm)[10]. The electron-hole pairs can only be created by the light whose wavelength is shorter than 387.5 nm. In this experiment, the value of band gap energy of pure TiO₂ shown in the figure 4 is fairly consistent with the above. The band gap energy of 0.03mol% Fe doped on TiO₂ is reduced to 2.8 ev (430.0 nm), showing that red shift occurred. It is thought that additional band gap energy was created by Fe doping so that electron-hole pairs can be excited in the visible light wavelength region and red shift occults is possible.

3.4. Effect of Fe₂O₃ dosage on catalytic activity

The catalytic activities of Fe₂O₃/TiO₂ nanocomposite catalysts prepared under the same conditions (containing 0.00mol%, 0.03mol%, 0.10mol% and 0.15mol% Fe₂O₃ respectively) are shown on figure 5. It can be seen that 0.03mol% Fe₂O₃ doped TiO₂ is more photoactive than any other samples. 0.1mol% Fe₂O₃ doped TiO₂ has high photoactivity in comparison with TiO₂, but 0.15mol% Fe₂O₃ doped TiO₂ has lower Fe₂O₃ doped TiO₂ than pure TiO₂.

The beneficial effect of Fe³⁺ may be explained as follows: 1) The ion radius of Fe³⁺ (0.063 nm)[11] is much closer to that of Ti⁴⁺ (0.068 nm)[12], so the Ti⁴⁺ sites could be easily substituted by Fe³⁺ ions; 2) The Fe²⁺/Fe³⁺ energy level lies close to Ti³⁺/Ti⁴⁺ level (figure 6), similar to anatase, thus photogenerated electrons are transferred from TiO₂ to Fe²⁺/Fe³⁺ energy level (Fe³⁺ + e⁻→Fe²⁺). Fe²⁺ can be an effective electron trap. Meanwhile, due to the energy level of Fe²⁺/Fe³⁺ being above the valence band edge of anatase TiO₂[13], Fe²⁺ can also be served as vacancy trap: Fe²⁺ + h⁺→Fe³⁺.

However, high doping concentrations are not desirable, because of the high possibility that both charge carriers (e⁻/h⁺ pair) will be trapped, and on the other hand, more doping agents reduce the number of active centers on the surface of TiO₂ catalysts.
Figure 5. Effect of Fe doping concentration on degradation of acrylic acid (SCFCT, °C).
(a) 0.00% Fe2O3/ TiO2; (b) 0.03% Fe2O3/ TiO2; (c) 0.10% Fe2O3/ TiO2; (d) 0.15% Fe2O3/ TiO2

Figure 6. Energy level diagram of Fe3+ in rutile.

It can be seen from table 1 that 0.03mol% Fe2O3/TiO2 nanocomposite photocatalyst has higher photoactivity than TiO2 and Fe2O3, both under the ultraviolet light and visible light. This result is constant with the result of Uv-Vis. It is also suggested that light condition plays a vital importance in the degradation of acrylic acid. The efficient application of solar spectra still need to be further investigated.

Table 1. Effect of different light conditions on photocatalytic degradation of acrylic acid.

| Light condition | no light/% | ultraviolet light/% | visible light/% |
|-----------------|------------|---------------------|-----------------|
| Fe2O3           | 0          | 30.13               | 19.34           |
| TiO2            | 0          | 44.25               | 14.30           |
| 0.03mol% Fe2O3/TiO2 | 0          | 60.13               | 37.78           |

3.5. Effect of calcination temperature on the catalytic activities

0.03mol% Fe2O3/TiO2 samples prepared by SCFCT were calcined at 500, 600 and 700 °C for 1 h respectively. The catalytic activities of the obtained catalysts were determined with photocatalytic degradation tests including 300 mg·L⁻¹ acrylic acid. The degradation rates are listed in table 2.

Table 2. Effect of calcination temperature on the photo-catalytic activitiesa, b, c

| Calcination temp. (°C) | Calcination time (h) | Degradation rate (%) |
|------------------------|----------------------|----------------------|
| Without calcination    | /                    | 55.8                 |
| 500                    | 1                    | 60.13                |
| 600                    | 1                    | 73.0                 |
| 700                    | 1                    | 46.75                |

(a) Concentration of acrylic acid: 300 mg·L⁻¹.
(b) Addition of catalyst: 1 g·L⁻¹.
(c) Reaction temperature: 25±1 °C.

It can also be found that the degradation rate increases with the increase of calcination temperature. Sample calcined at 600 °C has the highest activity. When the temperature raises up to 700 °C the activity decreases to 46.75%. Low catalytic activity at low calcination temperature is attributed to the covered active centers by some organic compounds such as alcohols and surfactants. With the increase
of calcination temperature, decomposition of the impurities will expose more active center on the surface, thus leading to improvement in the activity of the catalysts. However, when the calcination temperature is increased to 700 °C, a rapid particle growth from 15.8 nm to 27.3 nm is occurred. The growth of the powder particles leads to the decrease of the surface area and photo catalytic activity.

3.6. Effect of preparation methods on the catalytic activities

It is obvious that the catalyst prepared by SCFCT shows higher photocatalytic activity than that of prepared by TD as shown in figure 7. It is due to the interfacial force of the solvent, which leads to collapse of the cavity structure and aggregation of particles. And therefore, the particle size increases and cavity volume decreases. Correspondingly, the surface area and the photocatalytic activity are reduced. This phenomenon could be avoided in the preparation of aerogels obtained by SCFCT. At supercritical condition of alcohol, the solvent in the pores expands rapidly without interfacial force. The composite particles with good dispersity and small size lead to quantum size effect and improve the carriers transfer efficiency. Thus, the catalysts prepared through SCFCT show higher catalytic activity.

![Figure 7. Effect of different preparation methods of Fe₂O₃/ TiO₂ (0.03%) on photocatalytic property: (a) SCFCT ; (b) TD.](image)

![Figure 8. Effect of H₂O₂ concentration on the acrylic acid degradation rate.](image)

3.7. Effect of H₂O₂

Effect of amount (different volume percentages 0.00v%, 0.033v%, 0.167v%, 0.33v%, 0.66v%) of H₂O₂ on the photocatalytic degradation of acrylic acid suspensions is shown in figure 8. It is clear that the addition of H₂O₂ greatly enhance the degradation in comparison with nanocomposite photocatalyst alone. The mixture of 0.03mol% Fe₂O₃/TiO₂ and 0.167v% H₂O₂ can completely degrade the acrylic suspensions in 3 h. Adding H₂O₂ (lower than 0.167v%) could increase the degradation rate. This may be attributed to the enhancement of the initial concentration of hydroxyl radicals. At the same time H₂O₂ can capture one electron of the conduction band and produce the hydroxyl radical (figure 9), which hinders the electron–vacancy recombination rate and increase the rate of the photocatalytic process[14].

\[
\begin{align*}
H₂O₂ + hv & \rightarrow 2·OH \\
H₂O₂ + e⁻ & \rightarrow ·OH + OH
\end{align*}
\]

![Figure 9. Formation of hydroxyl radicals from H₂O₂.](image)

At high concentrations of hydrogen peroxide, the reactions shown in figure 10 will occur.
Figure 10. Consumption of hydroxyl radicals in excess.

\[
\begin{align*}
    \text{H}_2\text{O}_2+\text{OH} & \rightarrow \text{H}_2\text{O}+\text{HO}_2^- \\
    \text{HO}_2^-+\text{OH} & \rightarrow \text{H}_2\text{O}+\text{O}_2
\end{align*}
\]

3.8. Results for COD$_{Cr}$

As can be seen from table 3, after 3 h treatment with 0.03mol% Fe$_2$O$_3$/TiO$_2$ and 0.167v% H$_2$O$_2$, the COD$_{Cr}$ ($\eta_{\text{COD}}$) value of acrylic acid suspensions is reduced from 448.4 mg·L$^{-1}$ to 35.57 mg·L$^{-1}$ (or by 92.07%). The degradation rate determined by absorbency method is 100%. Both results indicate that almost the whole amount of acrylic acid is decomposed into H$_2$O and CO$_2$.

| Photocatalytic degradation time (h) | 0    | 3    |
|-----------------------------------|------|------|
| The COD value (addition of H$_2$O$_2$ 0.167%) (mg·L$^{-1}$) | 448.4 | 35.57 |
| Degradation rate ($\eta_{\text{COD}}$/%) | /    | 92.07 |
| Absorbency (A)                    | 1.243| 0.00  |
| Degradation rate ($\eta_{\text{COD}}$/%) | /    | 100.00 |

4. Conclusions

Anatase phase Fe$_2$O$_3$/TiO$_2$ nanocomposite photocatalysts can be obtained directly by SCFCT, indicating that drying and crystallizing process can be accomplished in one step. Moreover, SCFCT can inhibit effectively the phase transformation from anatase to rutile. The Fe$_2$O$_3$/TiO$_2$ nanocomposite photocatalysts prepared possess good dispersity, crystallinity and high catalytic activity both under the ultraviolet light and visible light. In addition, H$_2$O$_2$ plays a vital role in improving the efficiency of photocatalysts.

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