

Preparation and characterization of magnetically separable photocatalyst (TiO₂/SiO₂/Fe₃O₄): Effect of carbon coating and calcination temperature

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Abstract

TiO₂/SiO₂/Fe₃O₄ composite was synthesized by sol–gel technique for silica and titania coatings on magnetite core to enable recovery after photocatalytic degradation. Carbon coating was also carried out by calcination of TiO₂/SiO₂/Fe₃O₄ under nitrogen atmosphere in presence of PVA as a source of carbon to enhance the adsorption of organic compounds on catalyst surface and to get better activity. All prepared samples were characterized using EDX, CN analyzer, XRD, BET and SEM. Degradation of methyl orange dye was used to assess the photocatalytic performance of the prepared samples. Calcination temperature was found to affect rate of reaction because of the formation of rutile phase at high calcination temperature. Carbon coated samples unexpectedly exhibited lower rate of reaction at almost all calcination temperatures.

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1. Introduction

Synthetic dyes are extensively used in many fields of up-to-date technology, e.g., in various branches of the textile industry, in the leather tanning industry, in paper production, in agricultural research, in light-harvesting arrays and in photoelectrochemical cells [1]. Photocatalysis using titania as a catalyst provides a good tool for synthetic dyes decomposition due to its characteristics, e.g., high efficiency, low cost, chemical corrosion inertness, and long-term stability against photocorrosion and chemical corrosion [2]. The detailed mechanism of the photocatalytic process has been discussed extensively in the literature [3–7] and will be only briefly summarized here. Illumination of an aqueous TiO₂ suspension with irradiation energy greater than the band gap energy (E_{bg}) of the semiconductor ($h\nu > E_{bg} = 3.2$ eV in the case of anatase TiO₂) generates valence

band holes h_{cb}^+ and conduction band electrons e_{cb}^- (Eq. (1)):



The produced electrons and holes generates redox environment which is able to degrade pollutants present in aqueous medium.

Lower TiO₂ particle size is favorable in photocatalytic reaction due to the higher surface area provided. However, it is not favorable from the industrial point of view since it needs further costly step to recover the photocatalyst after treatment. The present study aims to prepare and characterize of TiO₂/SiO₂/Fe₃O₄ and C/TiO₂/SiO₂/Fe₃O₄ composites. Both of composites can be separated from medium after treatment by using magnetism. Presence of silica membrane is essential to reduce the negative effect of magnetite on photocatalytic activity [8]. Coating with carbon was supposed to provide catalyst with simultaneous adsorption and oxidation properties leading to enhancement of activity as described by Tao et al. [9].

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2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TTIP), tetraethyl orthosilicate (TEOS), ammonium hydroxide, ethyl alcohol, H₂O₂ (30%), and methyl orange (MO) dyes (Wako Pure Chemicals Co.) were of reagent grade and were used without any further purification. Magnetite (Fe₃O₄) of particle diameter less than 180 μm, purchased from Wako Pure Chemicals Co., was sieved to obtain 25–45 μm (effect of core diameter on photocatalytic activity will be reported elsewhere).

2.2. Preparation of silica coated magnetite particles (SF particles)

Coating of magnetite with silica layer was carried out by using seeded polymerization technique with a sol–gel reaction as described elsewhere [10–13]. The seeded polymerization technique is based on hydrolysis of an organometallic silica precursor (TEOS) in the presence of core particles (seeds) under alkaline conditions, where with controlled hydrolysis of TEOS, an M–O–Si chemical linkage is established between the surface of an inorganic oxide (M) and TEOS. This is followed by lateral polymerization, and finally formation of a three-dimensional network via siloxane bond formation (Si–O–Si), which produces a homogeneous silica coating [14].

2.3. Preparation of TiO₂/SiO₂/Fe₃O₄ particles (TSF particles)

Coating with titania was carried out using sol–gel technique. Gel was prepared according to the method described by R.S. Sonawane et al. [15]. TTIP was hydrolyzed with water and the resulting titanium hydroxide was washed thoroughly to remove alcohol formed in the hydrolysis. To this precipitate, suitable volume of aqueous H₂O₂ (15%) was added slowly and allowed to dissolve the precipitate completely. Then, SiO₂/Fe₃O₄ (SF) powder was added to the formed titanium peroxide sol and agitated by ultrasonic for 5 min to allow homogeneous distribution of SF powder inside the sol solution. Calcination was carried out at different temperatures for 2 h under nitrogen atmosphere to avoid oxidation of magnetite. For simplicity, samples are coded as TSF x , where x is the calcination temperature.

2.4. Preparation of C/TiO₂/SiO₂/Fe₃O₄ particles (CTSF particles)

Carbon coating and calcination of TSF composites to form CTSF were carried out simultaneously as described by Tryba et al. [16] but by using solution of PVA instead of powder to ensure homogeneous distribution of carbon on prepared samples. Carbon coating was performed by mixing TiO₂/SiO₂/Fe₃O₄ composites with PVA solution, as a source of carbon. After mixing, the mixture was heated at different temperatures for 2 h under nitrogen atmosphere. For simplicity, samples are coded as CTSF x , where x is the calcination temperature. The minimum

calcination temperature used was 550 °C to avoid formation of melted PVA layer on TSF particles since carbonization of PVA starts from 250 °C and completes around 500 °C [17]. This layer may separate the titania surface from the aqueous medium.

2.5. Characterization of prepared samples

All powders were examined by energy dispersive fluorescence X-ray spectrometer (Shimadzu EDX-800, Rayny series) for the determination of TiO₂, SiO₂ and Fe₃O₄ ratios while carbon content was determined using automatic high sensitive NC analyzer (Sumigraph NC-22A). X-ray diffraction (XRD, Rigaku miniflex with a graphite monochromator, Cu K α radiation) was used for the identification of the formed phases. The particle diameter was measured under scanning electron microscope (SEM, JEOL JSM-5200). The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of BET equation (Gemini 2360 surface area analyzer).

2.6. Photocatalytic activity measurements

Photocatalytic activities of the samples were evaluated by decomposition of MO in a batch mode. Two hundred milliliters photo-reactor (UVL-100HA, Riko Company) equipped with 100 W high pressure mercury lamp ($\lambda_{\text{max}} \approx 365$ nm) was used. 50 ppm MO solution was mixed with the composite to make TiO₂ concentration equals 500 ppm, stirred and aerated for 30 min prior to the experiment to allow adsorption of the dye on the catalyst surface. Then, the UV lamp was switched on to start photodegradation of MO dye. After definite irradiation times, suitable volumes of solution were sampled, then filtered to separate the photocatalyst. The filtered solution was analyzed by UV–vis absorbency on Shimadzu 1700 spectrophotometer at the wavelength of the maximum absorbency of MO dye to measure the remaining dye concentration. For catalyst reuse experiments, catalyst was separated using magnetism during sampling to avoid weight loss from experiment to another.

3. Results and discussion

3.1. Characterization

Chemical compositions and specific surface areas of prepared samples are presented in Table 1. There are no much differences in the compositions determined by fluorescence X-ray spectrometer since all samples passed on the same processes. In case of CTSF samples, there is a decrease in carbon content as calcination temperature increases; same behavior was also observed by Tryba et al. [16] during carbon coating of pure titania. Generally, surface areas of both TSF and CTSF decreased with the increase in calcination temperature as a result of growth of titania crystals and formation of rutile of less surface area [18,19] as can be observed from XRD results (Fig. 1). CTSF samples were found to exhibit slightly higher surface area stemmed from carbon layer.

Fig. 1 shows XRD patterns of TSF and CTSF composites calcined at different calcinations temperatures. All samples contain

Table 1
Chemical compositions and BET surface areas of TSF and CTSF composites calcined at different temperatures

Sample code	Calcination temperature (°C)	Chemical composition (wt%)				BET surface area (m ² /g)
		C ^a	TiO ₂ ^b	SiO ₂ ^b	Fe ₃ O ₄ ^b	
TSF250	250	0	41.2	17.3	41.5	34
TSF350	350	0	38.2	15.4	46.4	37
TSF450	450	0	41.9	14.4	43.7	37
TSF550	550	0	42.5	15.6	41.9	33
TSF650	650	0	37.9	14.6	47.5	31
TSF750	750	0	37.8	15.7	46.5	28
TSF850	850	0	37.1	17.6	45.3	26
TSF950	950	0	39.5	15.2	45.3	26
CTSF550	550	1	41.8	17.3	39.9	33
CTSF650	650	0.79	43.2	15.7	40.31	32
CTSF750	750	0.7	39	15.4	44.9	30
CTSF850	850	0.3	41.4	17.3	41	29
CTSF950	950	0.21	41.5	16.9	41.4	28

^a measured by CN analyzer.

^b measured by EDX.

three crystalline phases which are anatase and rutile for TiO₂ along with magnetite phase. No relevant peaks of SiO₂ were observed in the XRD patterns, which indicate that SiO₂ separates out on the surface of magnetite particles to form a very thin membrane but not integrates with itself to form larger crystals [8]. Pure anatase phase could not be obtained by this method of preparation. Complete phase transition could be observed at 750 °C in both cases, TSF and CTSF. Absence of ilmenite phase, which is usually formed due to reaction between rutile and magnetite at high temperature, reveals a good coverage of

magnetite with silica layer. Another proof of successive coating is that in case of CTSF composite elemental iron was not formed indicating separation of magnetite from carbon.

For quantitative determination of phase structure of titania in CTSF and TSF composites, the ratio between anatase and rutile, extracted from XRD charts, was calculated with the empirical formula (Eq. (2)) [2],

$$R(T) = 0.679 \left(\frac{I_R}{I_R + I_A} \right) + 0.312 \left(\frac{I_R}{I_R + I_A} \right)^2 \quad (2)$$

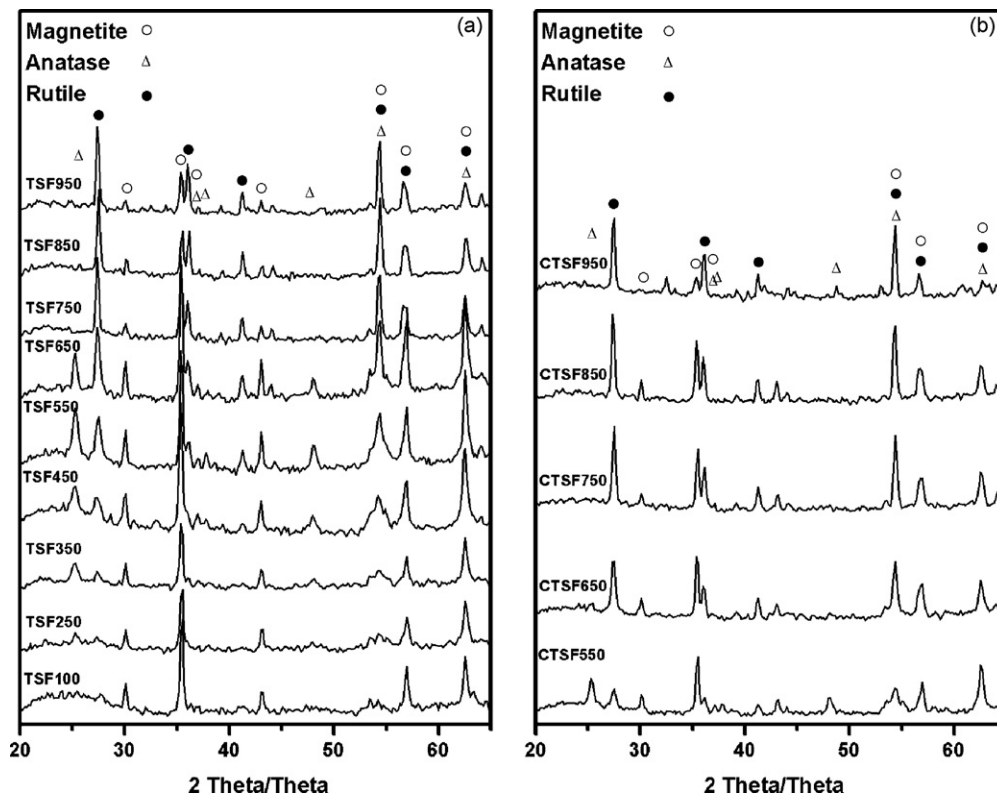


Fig. 1. XRD patterns of (a) TSF and (b) CTSF composites.

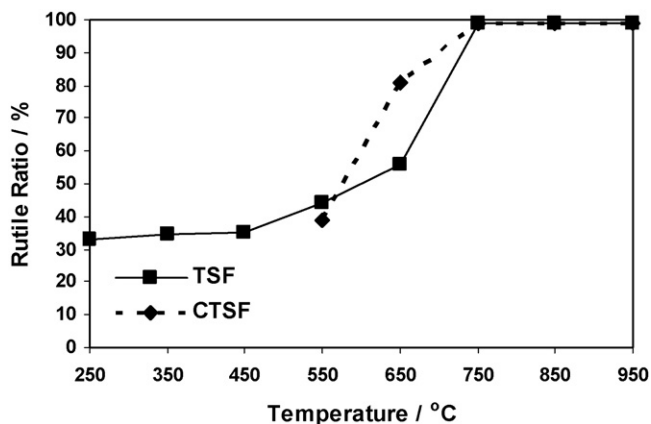


Fig. 2. Rutile ratio variation in TSF and CTSF composites calcined at different calcination temperatures.

where $R(T)$ is the percentage content of rutile at each temperature, I_A is the intensity for the main anatase reflection, and I_R is the intensity for the main rutile reflection after baseline correction. The calculated ratios of rutile phase are presented in Fig. 2.

In case of TSF, It was found that rutile ratio is constant until 450 °C was reached. Then, an increase in the ratio was observed and a complete phase transition occurred at 750 °C. In CTSF case, rutile ratio was increasing with the calcination temperature and the complete phase transition occurred at 750 °C similar to TSF composite. This result suggests that carbon coating does not significantly affect on the phase structure of titania.

Neither TSF nor CTSF showed significant change in particle diameter with calcination temperature as can be observed from scanning electron microscope images presented in Fig. 3. This might be due to the presence of titania as a membrane on SF particles. However, titania crystals grew and phase transition occurred during calcination step according to XRD data shown above. Conclusively, calcination temperature led

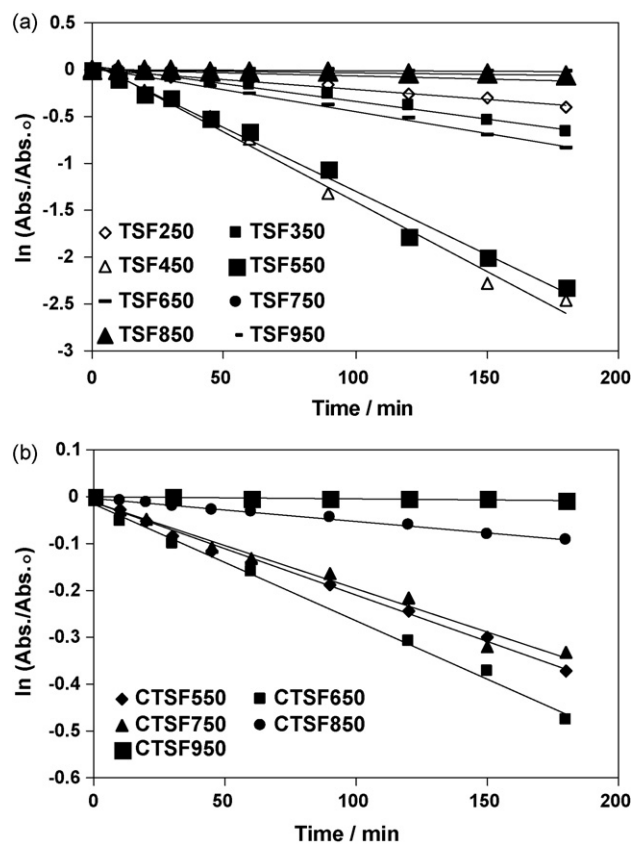


Fig. 4. Change in MO absorbance under photocatalytic degradation using (a) TSF and (b) CTSF composites.

to growth of titania crystals but did not lead to aggregation of particles.

3.2. Photocatalytic activity

Photocatalytic degradations of MO using TSF and CTSF are presented in Fig. 4. The change in absorbance with time appears

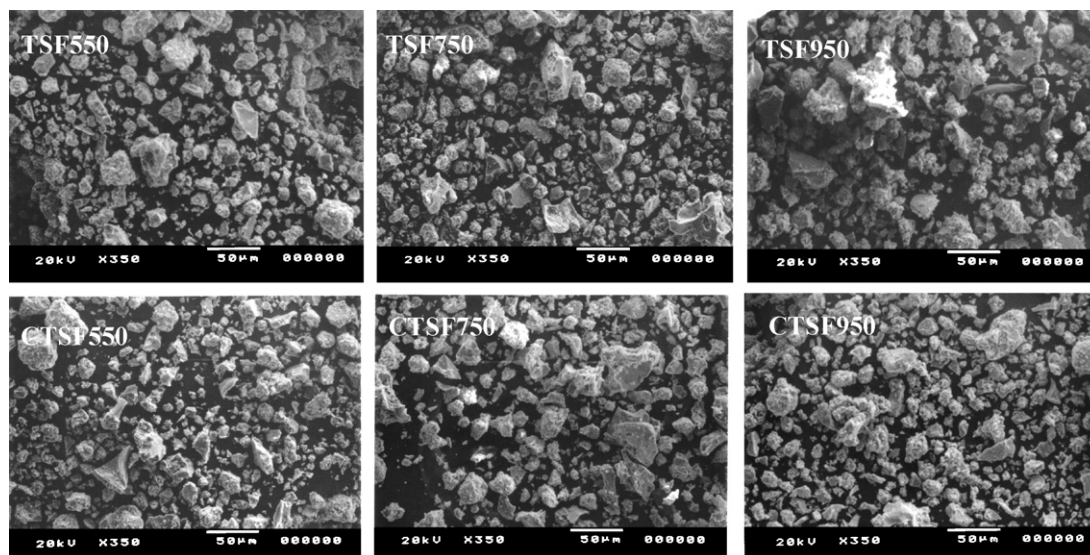


Fig. 3. Scanning micrographs of TSF and CTSF samples heated at different calcination temperature.

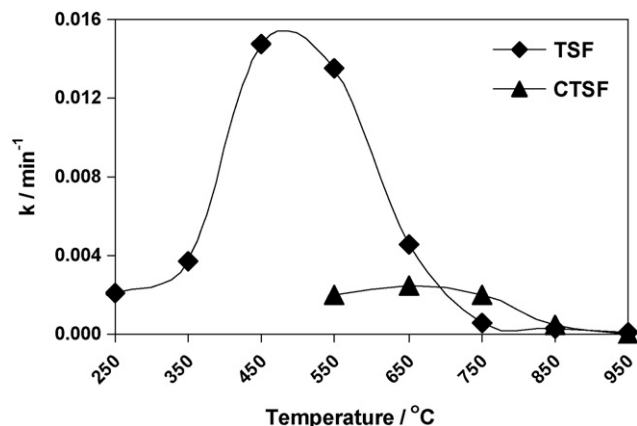


Fig. 5. Change in MO degradation rate with calcination temperature.

to follow pseudo first order kinetics for both composites. Effect of calcination temperature on reaction rate constant is shown in Fig. 5. In TSF, there is maximum activity at 450 °C, which can be explained on the basis of rutile to anatase ratio. The increase in calcination temperature causes increase in crystallinity of TiO₂, i.e., number of TiO₂ crystals increases as can be observed in Fig. 1. Both anatase and rutile peaks become higher as temperature increases. After 450 °C, rutile/anatase ratio increased leading to formation of more rutile of lower photocatalytic activity. CTSF samples have shown lower photocatalytic activity than TSF samples at almost all calcination temperatures. Since carbon does not affect on phase structure of titania, the lower activity of CTSF could be attributed to the black color of carbon layer that absorb most of UV light before reaching titania surface.

For the assessment of catalyst recovery, TSF450 sample was used in the degradation of different solutions of MO dye in three consecutive experiments. Catalyst was recovered using magnet during sampling and after each experiment. Variations of MO normalized absorbance with time during the three experiments are presented in Fig. 6. MO dye could be degraded efficiently within the first two runs. A loss of catalyst after second run might occurred leading to slightly lower reaction rate.

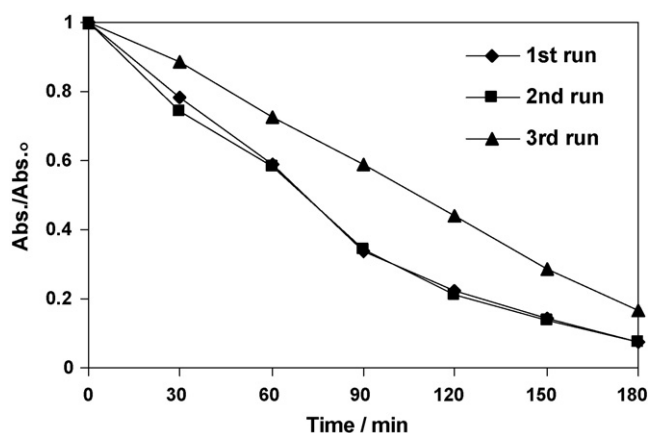


Fig. 6. Degradation of MO dye using TSF450 sample.

4. Conclusion

A TiO₂/SiO₂/Fe₃O₄ composite was synthesized by sol-gel technique for silica and titania coatings on magnetite core to facilitate catalyst recovery using magnetism. Carbon coating was carried out by heating TiO₂/SiO₂/Fe₃O₄ under nitrogen atmosphere in presence of PVA as source of carbon. Surface areas of both composites decreased with the increase in calcination temperatures due to the formation of rutile phase. Rate of methyl orange degradation was affected significantly by the calcination temperature as a result of transformation of anatase phase to rutile phase of lower activity. Regardless the small amount of carbon used, carbon coating was found to affect negatively on the rate of reaction which might be due to the dark color of carbon leading to absorption of UV light before reaching titania surface. TSF catalyst can be reused multiple times though small decrease in rate of MO degradation was observed and a more effective recovery method should be developed.

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