PREPARATION OF NANO $FETIO_3$-TIO_2 CATALYST FROM ILMENITE ORE FOR CATALYTIC DEGRADATION OF METHYLENE BLUE

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Abstract

Nano $FeTiO_3$-TiO_2 promises as a highly effective material for photo catalytic degradation of organic dye pollutants. Nano $FeTiO_3$-TiO_2 has been successfully prepared from ilmenite ore as raw material by simple modified sulfate route. The obtained low cost iron titania possesses high active surface and good Fenton-like catalytic activity evaluated by monitoring the degradation of methylene blue (MB) in the present of H_2O_2. The effect of acid concentration during synthesis on crystal structure, composition of composites and catalytic activity of the prepared samples was investigated and discussed. The crystalline structure and morphologies of prepared samples was investigated with X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM) coupled with EDAX, respectively. The adsorbed organic on samples surface were characterized by Fourier transform infrared spectroscopy (FTIR). The nano $FeTiO_3$-TiO_2 samples show significant effectiveness of catalyst under Fenton-like process due to the $FeTiO_3$ content obtained from natural iron in ilmenite ore, sulphate group on samples surface and high surface area.

Keywords: Ilmenite, catalyst, methylene blue, fenton, $FeTiO_3$

Introduction

Ilmenite ore ($FeTiO_3$) is an important raw material for titanium dioxide production due to cheapness and abundance in nature for the titanium source (Zhang *et al.*, 2011; Panigrahi *et al.*, 2013). Because of the attractively unique properties of nanoilmenite, it has received considerable attention for the utilization in wide range of applications such as

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supercapacitor (Tao *et al*., 2011), oxygen carrier (OC) in a chemical-looping combustion (CLC) reactor (Adánez *et al*., 2010), gas sensor, solar cells, chemical catalysts and photocatalysts (Lind *et al*., 2013; García-Muñoz *et al*., 2016; Halpegamage *et al*., 2015; Zhang *et al*., 2015; Truong *et al*., 2012). Catalytic performance for dye degradation activity of ilmenite has been of interest to study due to increasing impact in environmental concern. In catalysis process, ilmenite can produce the reactive oxygen species such as OH^- $OH^•$ radicals, superoxide ions ($O_2^{•-}$) and H_2O_2 by Advanced Oxidation Processes (AOPs) and Catalytic Wet Peroxide Oxidation (CWPO) or Fenton like reaction, which can be applied for degradation of hazardous chemical or pollutants compounds in water. The Fenton/Fenton-like method is well-known as one of the most low-cost AOPs and accordingly magnetic natural minerals catalyst for Fenton-like have gained considerable attention due to ease of separation and reusability, fast reaction and inexpensiveness.

Recently, many researchers have developed several routes to synthesize ilmenite utilized as catalyst for organic pollutant degradation. Synthetic bare ilmenite or modified natural ilmenite such as highly reduced ilmenite ore can be used as catalyst in Fenton like reactions for decomposition of many organic dyes, organic compounds such as phenols (García-Muñoz *et al*., 2016; García-Muñoz *et al*., 2016). Higher decomposition rate can be obtained from TiO_2-$FeTiO_3$, which can increase the phenol degradation rate under UV irradiation and additional H_2O_2, by accelerating the oxidation cycle of Fe^{2+} to Fe^{3+}(Tryba *et al*., 2015). Titanate nanofibers synthesized from ilmenite mineral showed significant enhancement in photocatalytic activity under UV light (Simpraditpan *et al*., 2013). Heterojunction of synthetic $FeTiO_3/TiO_2$ in the presence of H_2O_2 under UV–visible radiation showed noticeable improvement for organic dyes degradation activity (Orange G, 4-chlorophenol, Reactive Yellow RY 84 and Reactive Black RB5) by assistance of both mechanisms of TiO_2 photocatalysis and $FeTiO_3$ Fenton-like. Moreover, synergistic effect by charge transfer at the interface of $FeTiO_3/TiO_2$ could result to charge separation between two phases and suppressed charge recombination (Truong *et al*., 2012; Sivakumar *et al*., 2013; Marı´a *et al*., 2016). However, to remove organic pollutant by catalysis process, large scale of catalyst product is required and suitability of nanoilmenite preparation method is necessary and remains as a challenge. Preparation of nanoilmenite by use of ilmenite ore as starting material is one of the promising ways to solve this problem owing to reduction of the production cost in raw material and synthesis process. York R *et. al*, synthesized sulfated Fe_2O_3-TiO_2 from ilmenite ore as raw material by treatment with concentrated sulfuric acid and evaluated photocatalytic degradation activity by oxidation of 4-chlorophenol (4-CP). The present of Brønsted and Lewis acid sites at the surface of sulfated Fe_2O_3-TiO_2 samples led to favorable adsorption of organic molecule and dissolved oxygen in water, which resulting increasing reaction activity, since the reaction rate is control by surface phenomenon (York *et al*., 2010). Typically, starting raw ilmenite ore has naturally different phase structure from TiO_2 and Iron is a component in ilmenite ore that make it a promising candidate as a modified catalyst in Fenton-like reaction.

In this study, we prepared nano $FeTiO_3$-TiO_2 catalyst by facile modified synthesis method using ilmenite ore as raw material without the reducing step under high temperature. The effect of sulphuric acid concentration during synthesis of samples was studied. The catalytic efficiency of prepared samples was evaluated via Fenton-like reaction and discussed.

Experimental Details

Synthesis of Nano FeTiO$_3$-TiO$_2$ Catalyst

Ball-milled ilmenite ore were prepared by loading the mixture of 5 g ilmenite ore with 136 and 118 g of 2 and 5 mm-diameter zirconia ball in the milling cell and filled with 40 ml deionized water. The milling process was operated at room temperature for 24 h. The milled ilmenite in water is denoted as milled ilmenite. The nano $FeTiO_3$-TiO_2 catalyst prepared by mixing the 4 g of milled ilmenite with 100 ml sulphuric acid solution under constant stirred for 4 h at 80°C. The solid residue was washed with deionized water for several times then was dried at 100°C for 24 h.

The prepared catalyst samples with sulphuric acid concentration at 40, 50, 60, and 70% are denoted as 40I, 50I, 60I, and 70I, respectively.

Characterization

Particle size, morphology and surface topology of samples were observed by using SEM; EVO MA10 and for high magnifications using FE-SEM, JEOL JSM 6340F. XRD patterns for all samples were measured using X'Pert PRO PANalytical with 0.15405 nm Cu-Kα radiation source. Fourier transform infrared spectroscopy (FTIR, Shimadzu IRTracer-100) was employed to investigate the surface functional group adsorbent of prepared nano $FeTiO_3$ samples. The concentration of degraded MB solution was measured using a UV–vis spectrophotometer (UV-vis, Shimadzu UV-2401PC).

Fenton Reaction Experiments

The catalytic performance of the prepared nano $FeTiO_3$-TiO_2 samples was investigated via Fenton-like reaction to degrade 2 mg dm^{-1} of Methylene Blue (MB) aqueous solution. 200 mg of samples were mixed into 200 ml of dye solution and stirred for 30 min to achieve equilibrium dye adsorption before adding 3 ml of H_2O_2 into the suspension. Constant stirring was kept for 60 min before 4 ml of aliquots suspensions samples was collected at 10 min intervals for first 30 min to measure dye adsorption on the samples and at 5 min intervals until 90 min to determine MB degradation efficiency. Measurement of concentration of MB in each solution was conduction by mean of optical absorption in the wavelength ranging from 400 to 800 nm to evaluate the adsorption and degradation percentage of MB.

Results and Discussion

Surface Morphology Analysis

SEM images of starting ilmenite ore, milled ilmenite and prepared samples are shown in Figure 1 accompanying EDX spectra as the insets. High magnified FESEM images of the samples are exhibited in Figure 2. Particles size of the starting ilmenite is evaluated in the range of 100 to 200 μm. The particle size of milled ilmetnite was significantly reduced from ilmenite ore to be approximately 200 nm. The prepared 10I to 60I samples remain as small particle feature while the 70I sample show observable accumulation to form larger particle with average size around 5-10 μm. The element contents of prepared samples monitored by EDX analysis indicate the existence of titanium, iron and oxygen. The typical surface topology of prepared samples shows nanostructure with structure size around 20 nm after sulphuric acid treatment implying the great increase in specific surface area of the final product.

X-ray Diffraction

XRD patterns of the starting ilmenite ore clearly show ilmenite phase pattern [JCPDS 29-0733]. The milled ilmenite shows more amorphous feature implied by the increase of broadening of characteristic peak and decrease in peak height. The prepared 10I and 40I samples shows observable increase in crystallinity that is possibly owing to the fact that 10 to 40% sulphuric acid concentration can dissolve only small amorphous particle. For the higher concentration from 50 to 70%, it is found that increasing reaction of sulphuric acid with the milled ilmenite is favourable accompanying the XRD patterns showing features of higher amorphous pattern due to large amorphous surface area to mass ratio corresponding to FESEM images. XRD peaks of not well-crystallized sulfated ilmenite, situate between 2 theta degree of 30.5 to 32 appeared for the 50I, 60I, and 70I samples. The peak at 2 theta degree of 27.5 typically assigns to rutile TiO_2 (110) appeared in the 40I sample and increasing for 50I to 70I samples.

FTIR Analysis

FTIR spectra of milled ilmenite and prepared samples measured in wave number range between 600 and 1350 cm^{-1} are illustrated in Figure 4. The bands at around 600 cm^{-1} and 650 cm^{-1} are typically attributed to O-Ti-O bending and Ti-O stretching vibration, respectively and superposition on the Fe-O band characteristic. The presence of broad peak at around 1000–1300 cm^{-1} generally ascribes to characteristic of various sulfate species. Typical sulfate S = O stretching vibrations shows absorption frequencies at

1100–1200 cm^{-1}and around 1210–1240 cm^{-1}. Band located at around 1000 cm^{-1} to 1300 cm^{-1} also assigns to contribution of the symmetric stretching vibration of S–O bond, chelating bidentate coordination bond at surface corresponding to band at 1023 cm^{-1}, 1130 cm^{-1} and 1056 cm^{-1} (Fajardo *et al.*, 2010; York *et al.*, 2010; Scipioni *et al.*, 2014; Liu *et al.*, 2015; Miranda *et al.*, 2015; Zeng *et al.*, 2016). 10I to 70I samples demonstrate the bands of sulphate group while 50I and 60I show highest absorption bands and gradually decrease from 70I, 40I, and 10I, respectively. The milled ilmenite shows no absorption bands of sulphate group and 70I exhibits lowered sulphate group than 50I and 60I implying the lower reaction for high concentration at 70% sulphuric acid due to the tendency of particle accumulation.

Fenton-like Catalytic Activity

The catalytic activities of prepared samples were performed by evaluating the degradation of MB aqueous solution in the presence of H_2O_2, Fenton-like system. The concentration of MB aqueous solution was measured at a wavelength of 664 nm which is specific absorption of MB. The result shown in Figure 5 indicates that dominantly height adsorption and catalytic activity of 50I sample is obtained proving that the 50I performs superior catalytic activity. That is in harmony with the result of from FESEM and high sulphate surface content from FTIR. The adsorption-desorption shows an approach to equilibrium in 30 min for all samples and the MB degradation occurs at the Fenton-like reaction begin and the MB concentration

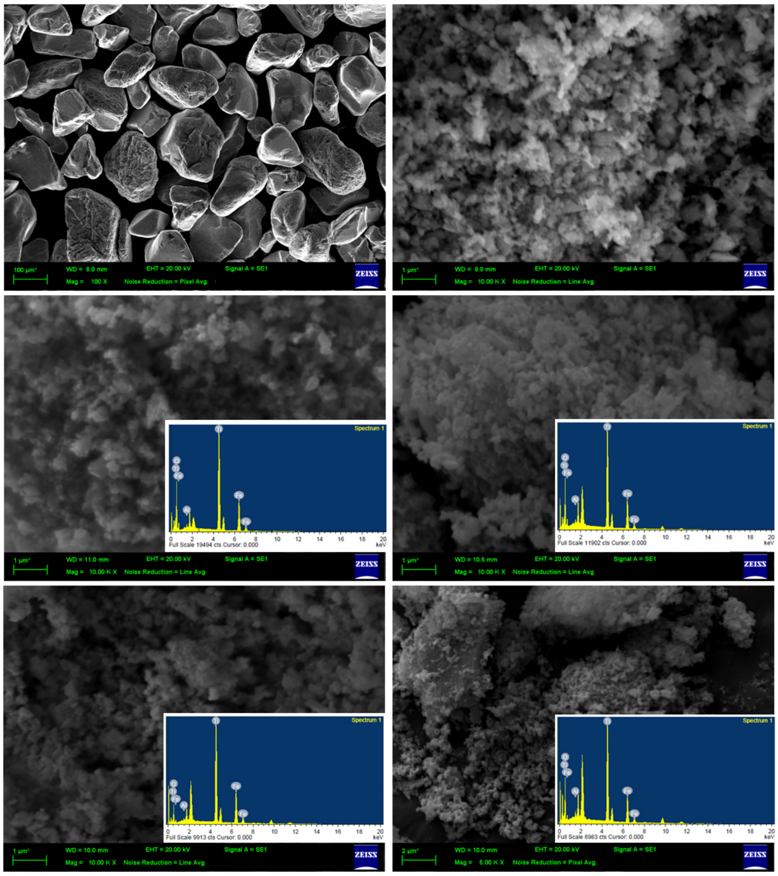

Figure 1. Typical SEM images of starting ilmenite ore, milled ilmenite, prepared 10I, 50I, 60I and 70I samples at different magnifications with EDX spectra

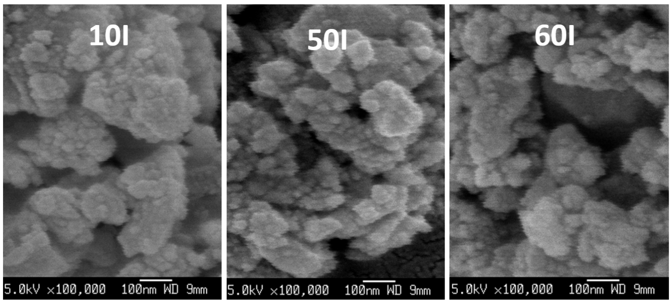

Figure 2. Typical FESEM images of prepared 10I, 50I and 60I samples

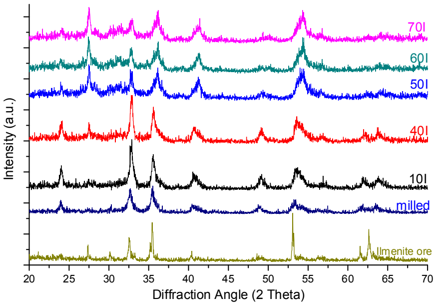

Figure 3. XRD pattern of starting ilmenite ore, milled ilmenite and prepared samples at different sulphuric acid concentration

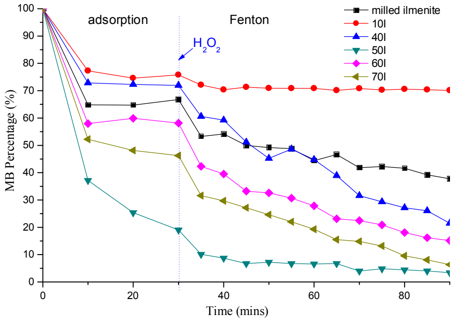

Figure 5. Fenton-like degradation of MB aqueous solution activity with the prepared catalyst samples from different sulphuric acid concentration

rapidly decreases again after 30 min. Catalytic performance and MB adsorption of 70I shows slightly greater catalytic performance than 60I that is reverse trend from the FTIR result. 40I and milled ilmenite perform lower efficiency and 10I showed lowest efficiency respectively corresponding to the results from FTIR.

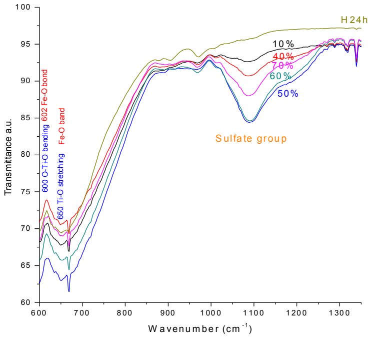

Figure 4. FTIR spectra of milled ilmenite and prepared samples analysed for 500 – 1350 cm^{-1}

The results from Figure 6(b) indicate that the MB adsorption-desorption for 50I tends to reach an equilibrium at 30 min. Comparing to the laboratory grade of $FeTiO_3$, TiO_2 anatase and TiO_2 P25. The TiO_2 anatase exhibits high MB adsorption, however, for the Fenton-like catalytic MB degradation activity, 50I sample shows best catalytic efficiency while $FeTiO_3$, TiO_2 anatase and TiO_2 P25 possess low activities.

Conclusions

Cost-effective nano $FeTiO_3$-TiO_2 AOP catalysts were successfully synthesized by using ilmenite ore as low-cost raw material. The prepared nano-ilmenite catalysts shows high performance in catalytic activity in degradation of MB dye via Fenton-like process. The maximum MB adsorption and MB degradation was obtained by 50I sample. This feature could occur at the catalyst interface while high adsorption would lead to high catalytic activity. The high surface

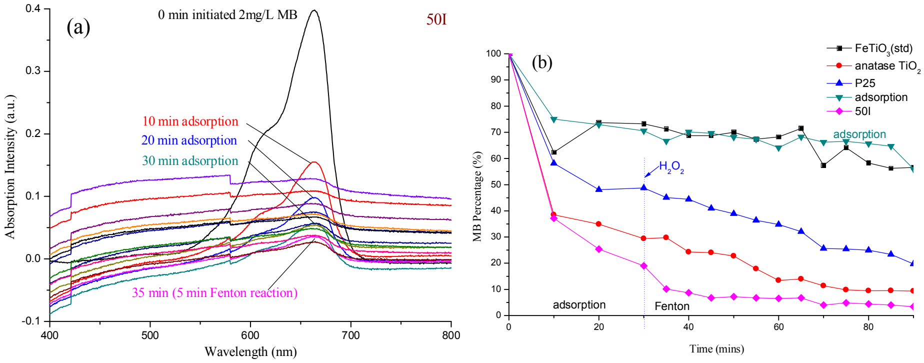

Figure 6. **Typical UV-vis spectra of MB degradation for 50I sample, Comparison MB adsorption and catalytic activity for Fenton-like reaction of 50I with $FeTiO_3$ (lab grade), TiO_2 anatase (lab grade) and TiO_2 P25**

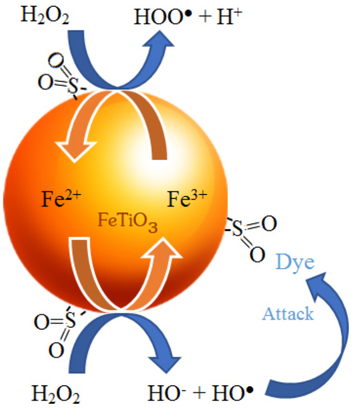

Figure 7. The propose mechanism diagram for prepared nanoilmenite catalytic samples by Fenton-like reaction

area with the sulphate group on ilmenite surface play significant role to accelerate catalytic activity and the corresponding catalytic mechanism on Fenton-like system could be proposed in Figure 7. In this work, the optimized condition was achieved from 50I. These cost-effective method and raw material can promise for beneficial development and application of organic pollutant wastewater treatment.

Acknowledgments

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