

Facile fabrication and characterizations of nanostructured Fe₂O₃-TiO₂ composite from Ilmenite ore

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Abstract— Fe₂O₃-TiO₂ nanoparticles promises as a highly effective material for adsorption of heavy metals and used as photocatalyst for the removal of organic dye pollutants. In this study, nanostructured Fe₂O₃-TiO₂ composite was successfully fabricated by one-step reaction of ilmenite ore at the high temperature in ambient condition. The resultant Fe₂O₃-TiO₂ composite was characterized by using X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherm. The effects of sintered temperature and time on the formation of the Fe₂O₃-TiO₂ nanocomposite were investigated in detail. The Fe₂O₃-TiO₂ was formed from ilmenite ore after calcination at the temperature of 700°C in 3 hours, followed by a ball-milled process in 4 hours. The obtained Fe₂O₃-TiO₂ composite has an average diameter of from 50 - 100 nm with the BET surface area of 7 m²/g.

Keywords—Ilmenite, Fe₂O₃-TiO₂, nanocomposite, mixed oxides, ore processing.

I. INTRODUCTION

In recent years, nanostructured Fe₂O₃-TiO₂ particles have been extensively studied by many researchers for application of photocatalytic oxidation¹⁻³ and adsorption processes.⁴⁻⁶ Various synthetic approaches for fabrication Ti /Fe oxides composites have been reported in the literature.^{1, 4, 7-8} One of the most employed methods to synthesize nanostructured Fe₂O₃-TiO₂ composite is co-precipitation. The co-precipitation technique is related to the dissolving of a salt precursor such as a chloride, oxychloride or nitrate. The precipitation of corresponding metal hydroxides is occurred during addition of base solution such as sodium hydroxide or ammonium hydroxide solution. The residues are then washed and calcined to obtain the final products. This preparation method is effective for synthesis of metal oxide composites. Other processes such as hydrothermal deposition,⁸⁻⁹ impregnation^{8, 10} and sol-hydrolysis⁹ have been also employed to improve the distribution of FeII/III

into the TiO₂ lattice. The sources of Ti and Fe in fabrication of mixed oxides composite have been utilized including titanium tetra-isopropoxide,^{8, 10} titanium IV tetra-tert-butoxide⁹ and powdered TiO₂ anatase as Ti pre-cursors and iron nitrate,⁸ FeIII acetylacetonate¹⁰ and FeII/III chloride as Fe pre-cursor materials.⁹

There are several parameters affecting to the formation of TiO₂ and Fe₂O₃ such as the use of synthetic method, calcination temperature and relative ratio of Ti and Fe oxides. For example, calcination temperatures of Fe:Ti (1:1 ratio) mixtures at 700°C and 900°C, lead to the information of rutile and of pseudo-brookite (Fe₂TiO₅) due to the diffusion of FeIII into TiO₂ at higher temperature whereas only amorphous anatase and traces of rutile were found at calcination temperature of 500°C.¹⁰

Ilmenite ore (FeTiO₃) is an important raw material for titanium dioxide production due to cheapness and abundance in nature for the titanium source.^{2, 11} Because of the attractively unique properties of nanoilmenite, it has received considerable attention for the utilization in wide range of applications such as supercapacitor,¹² oxygen carrier in a chemical-looping combustion reactor,¹³ gas sensor, solar cells, chemical catalysts and photocatalysts.¹⁴⁻¹⁸ Ilmenite ore has been employed to fabricate the Fe₂O₃-TiO₂ mixed oxides by many researchers.^{3, 19-22} Smith *et al.* successfully fabricated sulfated Fe₂O₃-TiO₂ by treatment of ilmenite ore with sulfuric acid and the prepared sulfated mixed oxides show the photocatalytic activity toward oxidation of 4-chlorophenol (4-CP) in aqueous medium under UV-vis and visible light irradiation.²² The same procedure was also employed to synthesize sulfated Fe₂O₃-TiO₂ and used as a catalyst for conversion of vegetable oil to biodiesel.³ Recently, nano FeTiO₃-TiO₂ had been successfully prepared from ilmenite ore as raw material by simple modified sulfate route.¹⁹ This nano FeTiO₃-TiO₂ samples showed significant effectiveness of catalyst under Fenton-like process. However, most of these Fe₂O₃-TiO₂ composites prepared from ilmenite ore contains sulfate groups and related to toxic fabricating process (treatment

with concentrated acid). In order to address these disadvantages, we present a facile approach to fabrication of nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite from ilmenite ore by calcinating of raw ilmenite ore at high temperature and followed by a ball mill process. The prepared $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite are thoroughly characterized by XRD, SEM, FTIR, and BET. The The effects of calcination conditions are also studied in detail.

II. EXPERIMENTAL SECTION

Synthesis of nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite

In the typical procedure, 10g of raw ilmenite ore 52% was washed with 100 ml sulfuric acid several times. The $\text{Fe}_2\text{O}_3/\text{TiO}_2$ mixed oxides were prepared by sintering 10 g of washed ilmenite at various temperature of 500, 600, 700, 800 and 900°C in different periods of time in air condition. The calcinated products were then cooled naturally to room temperature before underwent a ball-milled process with 150 and 200 g of 2 and 5 mm-diameter zirconia ball in the milling cell and filled with 80 ml deionized water. The milling process was operated at room temperature for 24 h. The milled $\text{Fe}_2\text{O}_3/\text{TiO}_2$ mixed oxides were filtered and dried at temperature of 60°C for 12 h to obtained nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite.

Characterization

Particle size, morphology and surface topology of samples were observed by using a Hitachi S-4600. The surface area was evaluated from the N_2 adsorption isotherm at 77 K using a BET TriStar II Plus 377. XRD patterns for all samples were measured using X'Pert PRO PANalytical with 0.15405 nm Cu-K α radiation source. Fourier transform infrared spectroscopy (FTIR, TENSOR II, Bruker) was employed to investigate the surface functional group adsorbent of prepared nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite samples.

III. RESULTS AND DISCUSSION

Illustrated in Figure 1 is the XRD patterns for the Ilmenite ore and the $\text{Fe}_2\text{O}_3\text{-TiO}_2$ mixed oxides obtained from calcination of ilmenite ore at temperature of 700°C in 3 hours. In the XRD pattern of ilmenite ore, all diffraction peaks were assigned to the Ilmenite (FeTiO_3) phase (JCPDS card No. 98-010-4235). After sintering at 700°C in 3 hours in air condition and followed by ball mill process, FeTiO_3 completely converted to $\text{TiO}_2/\text{Fe}_2\text{O}_3$ mixed oxides, which is clearly shown in the XRD pattern. All diffraction peaks in the XRD pattern of prepared $\text{TiO}_2\text{-Fe}_2\text{O}_3$ were denoted to the TiO_2 rutile (JCPDS card No. 98-006-2553) and Fe_2O_3 (hematite, JCPDS card No. 98-005-3677) phases.

The formation of $\text{TiO}_2\text{-Fe}_2\text{O}_3$ mixed oxides was further confirmed by FTIR spectrum. Figure 2 shows the FTIR

spectra of Ilmenite ore and the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ mixed oxides obtained from calcination of ilmenite ore at temperature of 700°C in 3 hours. In these spectra, the large and broad absorption peak at 3432 cm^{-1} is related to the stretch region of the surface hydroxyl groups with hydrogen bonds and chemisorbed water.²³⁻²⁴ The

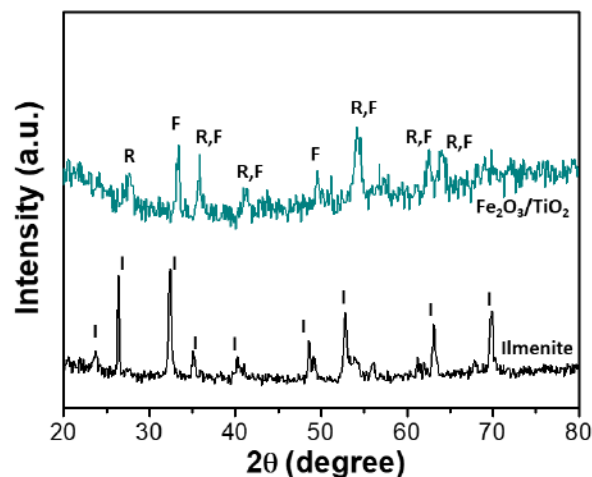


Fig. 1: XRD patterns of Ilmenite ore (black line) and as-prepared $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composites (blue line). The peaks are indexed with standard JCPDS cards, I – Ilmenite ore, R – Rutile, F – Fe_2O_3 .

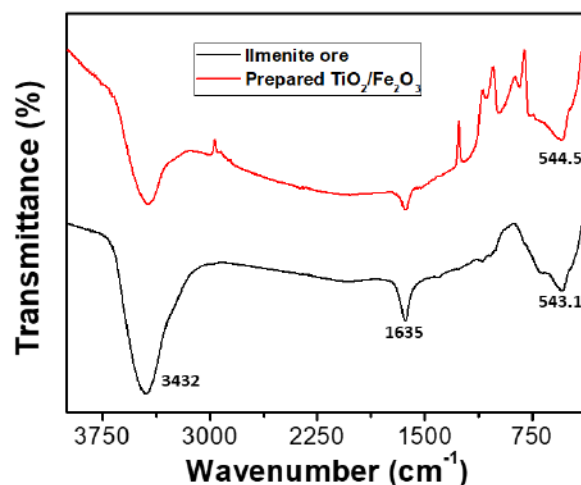


Fig. 2: FTIR spectra of Ilmenite ore (black curve) and as-prepared $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composites (red curve).

broad absorption peak at 1635 cm^{-1} can be assigned to the O–H bending of molecularly physisorbed water.²⁵ In the FTIR spectrum of ilmenite ore (black curve), the absorption peak at 543.1 cm^{-1} can be attributed to the Fe–O bond in the ilmenite (FeTiO_3).²⁶ A broad absorption peak at around this position was also observed in the FTIR spectrum of the prepared mixed oxides, which indicate the presence of the F–O sketching. However, this absorption peaks was at higher wavenumber of 544.5 cm^{-1} comparing to that of ilmenite, which indicates the formation of Fe_2O_3 . In the FTIR curve of mixed oxides, the appearance of the

large absorption in the range of 600 cm^{-1} to 800 cm^{-1} , which is characteristic of the O–Ti–O bond,²⁴ confirm the formation of TiO_2 oxide. The above results indicate that under the high temperature of 700°C in the ambient condition, the FeTiO_3 reacted with oxygen to form Fe_2O_3 and TiO_2 oxides.

The surface morphology of nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite was investigated by using scanning electron microscopy. Illustrated in Figure 3 is the SEM images of raw ilmenite ore and the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composites

obtained from calcination of ilmenite ore at 700°C in 3h and followed by a ball-milled process for 8 hours. The figure 3A shows that ilmenite ore is in form of microparticles with the diameter ranging from $100 - 500\text{ }\mu\text{m}$. After formation of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ oxides, the particle sizes are significantly decreased with particle diameter down to $50 - 100\text{ nm}$. This result indicates that the nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite was successfully fabricated from ilmenite microparticles by simple calcination and ball-milled approach.

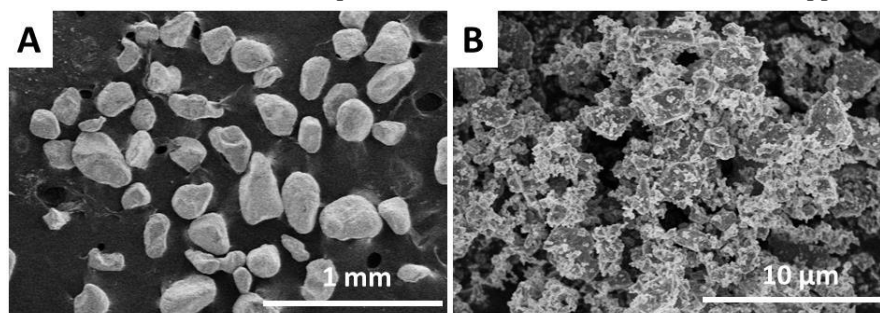


Fig.3 :SEM images of Ilmenite ore (A) and as-prepared $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composites (B)

The total surface areas of the nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite were obtained with reference to the Brunauer–Emmett–Teller (BET) multi-point and single-point methods [35] using the N_2 adsorption/desorption isotherm data. All samples were pretreated with degassing at 90°C for 1 h followed by 105°C overnight with ultra high purity nitrogen purge before the measurement. The pore volume data were calculated by using BJH method which is the procedure for calculating pore size distribution using the Kelvin equation and DH methods. Figure 4 shows the N_2 adsorption/desorption isotherm plot and inset is the BET surface area plot. The parameters of BET surface area analysis are summarized in Table 1. It is clear from the table that the obtained $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite has the BET surface area of $6.9645\text{ m}^2/\text{g}$ with pore volume of $0.023686\text{ cm}^3/\text{g}$ and the pore size of 15.7380 nm .

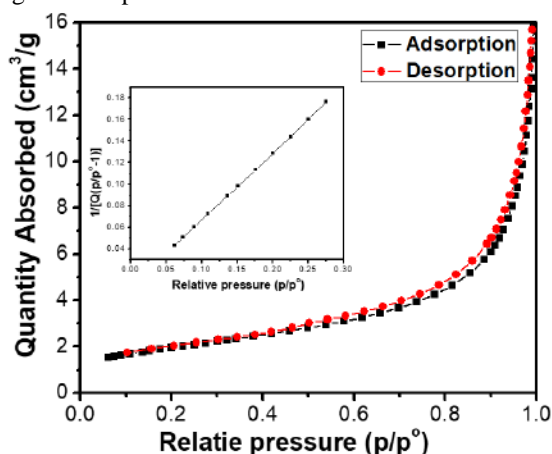


Fig.4 :Nitrogen adsorption plot and inset is the BET surface area plot

Table 1: BET surface area values

Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
6.9645	0.023686	15.7380

The effect of the sintering temperature on the formation of nanostructure $\text{TiO}_2\text{-Fe}_2\text{O}_3$ composite was investigated by employing the X-ray diffraction pattern. Figure 5 shows the XRD patterns of products obtained from the calcination of ilmenite ore at various temperature in 3 hours. In the XRD pattern of ilmenite sintered at the sintered temperature of 500°C , all diffraction peaks were consistent with ilmenite phase (JCPDS card No. 98-010-4235), which indicates that no oxides were formed from FeTiO_3 under this temperature. When the sintered temperature was further increased to 600°C , the diffraction peaks in the XRD pattern show the presences of TiO_2 (rutile) and Fe_2O_3 (hematite) phases. There still exists the diffraction peaks of ilmenite phase. However, no diffraction peaks of ilmenite was observed when calcined ilmenite at temperature of 700°C , which indicates that FeTiO_3 completely reacted with oxygen to form $\text{TiO}_2\text{-Fe}_2\text{O}_3$ mixed oxides. When calcined temperature was further increase to 800°C , diffraction peaks were assigned to the formation of TiO_2 (rutile), Fe_3O_4 (magnetite), and Fe_2TiO_5 (pseudobrookite) (JCPDS card No. 98-001-2310, 98-010-8716, and 98-001-2289, respectively). Interestingly, at the higher calcined temperature, all diffraction peaks was denoted to the Fe_2TiO_5 (pseudobrookite) phase, which shows that at this temperature FeTiO_3 reacted with oxygen in air to

form Fe_2TiO_5 . From these results, the calcined temperature of 700°C was selected as optimized temperature to obtain $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite from ilmenite ore.

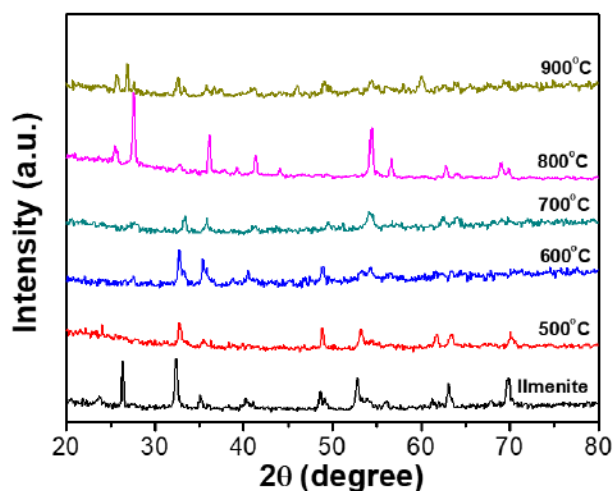


Fig.5 : XRD patterns of ilmenite ore sintered in 3h at various temperatures in air condition.

The sintered time also greatly affects to the formation of $\text{TiO}_2\text{-Fe}_2\text{O}_3$ composite. Figure 6 exhibits the XRD patterns of ilmenite calcined at temperature of 700°C in different period of time. After only 30 minute of calcination, majority of the ilmenite already converted to TiO_2 and Fe_2O_3 . This indicates that reaction of ilmenite with oxygen to form oxides at this temperature occurred

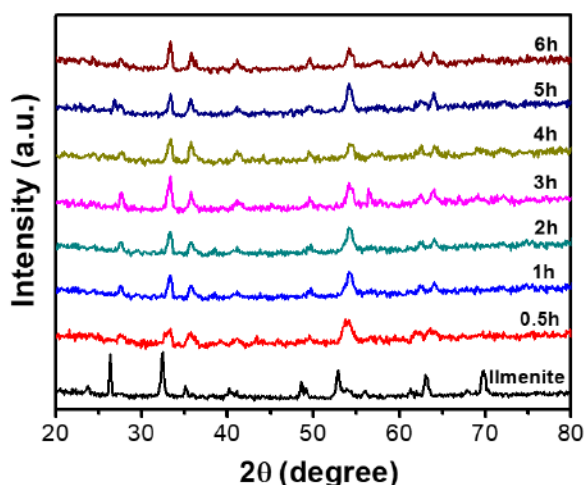


Fig.6 : XRD patterns of ilmenite ore sintered at temperatures of 700°C in various time points in air condition. relatively quick. It is obvious from the XRD patterns that further increase of the sintering time did not significantly affect to phase of the calcined product, the phase and crystallinity of the mixed oxides were almost unchanged after 2 hours of the calcination time.

IV. CONCLUSION

In summary, we have employed a simple one-step approach for successful fabrication of nanostructured $\text{Fe}_2\text{O}_3\text{-TiO}_2$ composite. The $\text{Fe}_2\text{O}_3\text{-TiO}_2$ nanocomposite was synthesized from ilmenite ore by calcination at the temperature of 700°C in 3 hours, followed by a ball-milled process in 4 hours. The obtained $\text{Fe}_2\text{O}_3\text{-TiO}_2$ composite has an average diameter of from 50 - 100 nm with BET surface area of around $7 \text{ m}^2/\text{g}$. While temperature greatly affects to the formation of $\text{Fe}_2\text{O}_3\text{-TiO}_2$ nanocomposite from ilmenite ore, the sintering time does not significantly affect to the formation of nanocomposite. The success of fabrication of nanostructured $\text{Fe}_2\text{O}_3\text{-TiO}_2$ composite from ilmenite ore by a simple approach of calcination will certainly introduce a cost-effective way to synthesize the metal oxides nanocomposite, which can be use in adsorption, photocatalysis and energy storage. In the next study, we will investigate the photocatalytic activity and adsorption properties of this resultant nanocomposite.

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