Characterization and x-ray absorption spectroscopy of ilmenite nanoparticles derived from natural ilmenite ore via acid-assisted mechanical ball-milling process*

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Abstract
In this work activated ilmenite nanoparticles were prepared by chemical-assisted in mechanical ball-milling process from ilmenite ore as starting raw material. The effect of milling process on their phase composition, particle size, surface morphology and local structure were investigated. Phase identification and crystalline structure of ilmenite mineral, milled samples and subsequent leached residues were characterized by x-ray diffraction (XRD). Meanwhile, the distorted octahedral structure and the oxidation state of relevant elements in ilmenite ore and activated ilmenite obtained by different process conditions were analyzed by x-ray absorption spectroscopy (XAS). Particle size and morphologies of the samples were monitored by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). Three dominant peaks of TiO2 rutile, FeTiO3, and Fe2TiO4 are obviously adulterated in XRD patterns after mechanical milling with water and acid solution when comparing to precursor mineral. However, the contaminated phase of FeTiO3 and Fe2TiO4 was readily decreased by acid-assisted mechanical ball-milling. The enhancement in leaching process of ilmenite residue after milling can be obtained with sulfuric acid. This result suggests that iron contaminated phase could be leached from the sample resulting to the decrease in Fe environment around Ti atom.

Keywords: ilmenite, FeTiO3, TiO2, acid-assisted mechanical ball-milling
Classification numbers: 2.03, 4.02, 4.03, 4.04, 5.00

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1. Introduction

Titanium dioxide (TiO₂) has been attractively attended as a highly functional material in various communities. Due to its unique feature in electrical and optical properties, the interest of TiO₂ material has been introduced in various fields of high value technologies, such as photovoltaic devices, electronics device, and catalysts [1–9]. Meanwhile, the commercial TiO₂ powder has mainly been utilized in whitening pigment and daily products including paint, paper, plastic, food, cosmetics, and inks [6–10]. Therefore, TiO₂ is certainly recognized as an important material that is essential in various technologies and economic affairs. The syntheses of TiO₂ from titanium sources via different processes are also costly and require precise conditions. Mainly, the titanium sources in natural solid ore are well known in rutile, leucoxene, and ilmenite. Among of them, ilmenite is one of the most important titanium minerals for the production of titanium dioxide and titanium metal [11]. Moreover, ilmenite ore is cost-effective for TiO₂ source and abundant distribution in many areas. Generally, TiO₂ product form ilmenite ore is approximately 40–65% depending on the geological origin. Main composition of ilmenite is naturally composed of the compound of titanium–iron mineral in chemical formula of FeTiO₃. Therefore, ilmenite is an interesting material for study of its prominent properties especially magnetic, electric and photocatalytic properties [1–9].

Currently, the metallurgical process for TiO₂ product from ilmenite is appropriate in industrial section via acid leaching process. Two commercial processes for mineral leaching are the chloride process and the sulphate process due to its strong incursion on mineral surface [6–9, 12–16]. The chloride process is a commonly used for TiO₂ production in industry which suitably treated on high quality sources of TiO₂ such as rutile, upgrading ilmenite, synthetic rutile and titanium slag. Therefore, Ti-enriched feedstocks with high TiO₂ contents are proper in the chloride process. For the sulphate process, it is suitably employed on low titanium content resources as ilmenite. Some researchers reported that lower acid concentration could be operated in mineral digestion which related to the reuse of waste acid and the decrease of acid waste emission [16, 17]. Ilmenite ore is leached by sulphuric acid to obtain the main compound of the iron titanium sulfate and oxysulfate. Removing iron sulphate from the solution is followed by hydrolysis reaction to obtain the final product of TiO₂ and H₂SO₄. Meanwhile, mechanical ball-milling process is one of effective methods for cooperating with acid leaching process for the activation of ilmenite ore due to low-cost, room-temperature-operation and suitability for industrial scale. Based on this fact, acid leaching process accompanying mechanical milling and for TiO₂ production from ilmenite ore is of interest and practical due to the overall leaching limiting control by surface chemical reaction [17–23]. It is believed that the particle size and crystalline structure of ilmenite ore can be changed after ball-milling process relating to the increase of active site surface area and lattice strain. In this work, the improvement of leaching process can be obtained owing to active reaction with acid. In typical early studies, an effect of mechanical milling activation and subsequent sulphuric leaching in sulphate base process efficiency has been investigated on activated ilmenite products residue by XRD and electron microscopy [13–16]. The acid-induced dissolution behaviour of ilmenite typically correlates to local structure at particle surface such as surface terminal texture of crystal structure, structural disorder, lattice stress and strain induced by mechanical milling activation. The change in local structure of titanate during ball-milling process is important especially in part of amorphous phase that could be evaluated by x-ray absorption near edge spectroscopy (XANES) study [24, 25]. However, based on our recent knowledge, the local structure evolution on ball-milled ilmenite ore has been rarely reported. In this present work, the developed acid-assisted mechanical ball-milling was introduced to synthesize nanoparticles from natural ilmenite ore. Physical structures of the milled ilmenite products were monitored by FESEM and TEM. Meanwhile, their crystal structures were characterized by XRD and the information of oxidation states, local structure and environment around the designated atoms relating to Ti and Fe atom can be achieved by XANES via the interpretation of pre K-edge absorption energy and fingerprint pre edge shape.

2. Experimental

2.1. Materials

Ilmenite ore was obtained from Sakorn Minerals Co., Ltd, Thailand. Ilmenite reference material (iron(II) titanate FeTiO₃ 100 mesh 99.9%) from Sigma-Aldrich and 95% sulfuric acid (analytical grade) from Fisher Scientific were used as starting materials.

2.2. Mechanical ball-milling process for ilmenite ore

Starting ilmenite was loaded in 50 ml of 10% sulfuric acid. After that, ilmenite suspension was grounded in a horizontal tumbler ball-mill reactor operated at 200 rpm for 24 h at room temperature. The zirconia balls with diameter of 2 and 5 mm were filled into 100 ml milling reactor at mass ratio of ilmenite and ball of 1:40 and stoichiometric mole ratio of ilmenite to acid solution of 1:3 mole. Meanwhile, DI water was used in the mechanical activation of ilmenite via ball-milling operation comparing to acid solution. Finally, the solid residue after milling process was separated from the mixture by centrifuge. The obtained milled ilmenite products from the mechanical ball-milling with DI water and mechanical ball-milling with sulfuric acid are designated as Milled-I and Acid milled-I.

2.3. Milled ilmenite ore with acid leaching process

Two grams of acid milled-I sample was subsequently used in acid leaching process using 100 ml 50% sulfuric acid operated at 95 °C for 6 h under continuous magnetic stirring. The solid residue was separated from slurry sample by centrifuge and washed with DI water for several times. The subsequent acid leaching of Milled-I is denoted as Leach-M. All of prepared solid residues were dried at 100 °C for 6 h prior to
characterization. A schematic of sample preparation is illustrated in figure 1.

2.4. Characterization

Surface and structural morphologies were studied using SEM; EVO MA10 for the higher resolution using FESEM (Hitachi-S4700) and TEM (Philips-Tecnai 12). Phase identification of starting ilmenite ore and as-prepared samples were characterized by XRD (X’PERT PRO, PANalytical) using Cu-Kα radiation source with a scan rate of 2° min⁻¹. XAS of Ti K-edge (4966 eV) and Fe K-edge (7112 eV) were recorded in transmission and fluorescence mode using Ge (220) double-crystal monochromator at the beamline 8 of the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand, with the storage ring running at 1.2 GeV and beam current of 80–126 mA during all measurements. For XANES evaluation, each spectrum was determined using an average over three independent scans. For comparison, XANES measurements were also performed on the standard powders including titanium metal, TiO₂ with anatase phase, TiO₂ with rutile phase, ilmenite reference, FeO, Fe₂O₃ and Fe₃O₄. Background removal and normalization of the XANES spectra was carried out using the ATHENA software.

3. Results and discussion

3.1. Surface morphology analysis

SEM images of as-received ilmenite ore and the residue of ilmenite milled in water (Milled-I) and acid (Acid milled-I) are shown in figure 2. For starting ilmenite ore as observed in figure 2(a) and the enlargement of particle figure 2(b), large particle with smooth surface of ilmenite mineral in the range of 100–150 μm can be observed. After mechanical milling process in water and acid, the size of leached residue of ilmenite powder can be reduced to be approximately 50–500 nm with irregular shape as illustrated in figures 2(c)–(f). Therefore, acid leaching route is necessary to extract pure TiO₂ phase from fragile mineral after mechanical process. Figures 2(g) and (h) indicate the agglomeration of Leach-M corresponding to the sulphate salt as observed in previous reports [15, 19]. Meanwhile, TEM images as illustrated in figure 3 reveal that the Acid milled-I sample (figure 3(b)) is smaller in its size than Milled-I sample (figure 3(a)). The particle of acid-assisted mechanical ball-milling sample is reduced to approximately 20 nm comparing to milling in pure water. Moreover, the particles of subsequent Acid milled-I by acid leaching (Leach-AM) is distinctly decreased and well dispersed as shown in figures 3(c) and (d). From these results, it can be interpreted that small particle size of ilmenite mineral is caused by the effect of acid-assisted mechanical ball-milling process, that relating to facile acid treatment in mineral digestion without any evident showing sulphate salt-like feature at the surface of the particles [15, 19].

3.2. X-ray powder diffraction analysis

XRD patterns of starting ilmenite ore, the residue of ilmenite milled in water and acid, and subsequent acid leached samples are given in figure 4. For as-received ilmenite ore, three dominant peaks of FeTiO₃ (ilmenite) (JCPDS No. 89-2811), Fe₂TiO₄ (titanomagnetite) (JCPDS No. 75-1378) and TiO₂ rutile, are obviously noticed in XRD patterns. The small amount of second phases is associated to TiO₂ anatase and Fe₂TiO₄ (pseudobrookite) (JCPDS No. 76-1158). The weaken broad peaks of milled ilmenite are occurred due to small particle size of ilmenite residue after milling which is consistent with the results of SEM image indicating the reduction of particle size in the product. Furthermore, the magnified XRD peaks reveal an increase in peak broadening with a shift toward higher 2θ values of FeTiO₃ peaks as shown in figure 4(b). The broadening XRD peak probably attributes to the decrease in crystallite size of the samples. The peak shift toward higher 2θ degree could be due to the increase in strain and lattice distortion. The crystallite size of milled ilmenite powder with sulfuric acid was decreased comparing to the sample milled with DI water that is in harmony with the result monitored by TEM images. These results indicate that FeTiO₃ and Fe₂TiO₄ phase can be readily decreased by mechanical ball-milling assisted with acid solution. Meanwhile, the enhancement in chemical reaction in leaching process of ilmenite residue can be quickly occurred due to small particle size relating to high surface area per volume to be corroded with sulfuric acid. The Leach-M sample also shows high intensity of TiO₂ and FeTiO₃ phases. This feature may be caused by the presence of sulphate salt at surface that can prevent the chemical surface reaction. This occurrence is supported by the existence of the sulphate salt XRD pattern (labelled as (+) in figure 4(a)) and SEM images (figures 2(g) and (h)) [20]. The presence of rutile TiO₂ and Fe₂TiO₃ phase is greatly reduced after leaching process of Leach-AM. These results are supported by TEM images showing the aggregation of fragile powder after complete acid-assisted mechanical process.

3.3. X-ray absorption analysis

The Ti K-edge x-ray absorption of titanium metal reference, TiO₂ anatase reference, TiO₂ rutile reference, ilmenite reference, as-received ilmenite ore, Milled-I, Acid milled-I and
Leach-AM are shown in figure 5. The K-edge absorption energy values were determined by the maximum value of the first derivative. Figure 5(b) shows the corresponding first-order derivative XAS. The spectra of Ti near-edge region and white lines shown in figure 5 can be ascribed to the electron transition from $1s$ orbital to $4p$ orbital in continuum states [24, 26–30]. Ti K-edge absorption energy of the ilmenite phase (ilmenite standard and ilmenite ore) is 4977 eV [31] apparently at lower energy than rutile TiO$_2$ reference due to the presence of Fe–O–Ti linkage of FeTiO$_3$ [32, 33] and contribution of Fe$_2$TiO$_4$ phase [34]. Ball-milled ilmenite in DI-water presents slightly increasing edge energy shift toward TiO$_2$. This occurrence may be due to crack of FeTiO$_3$ or other iron titanate crystal phase with the small size effect increasing the surface area of unsaturated coordination atom at the particle surface layer. The coordination of atom at surface is considerably different from the bulk that can induce interior lattice layer from surface disorder. Regarding to the XRD results, ball-milling may significantly contribute distortion and/or defect and low crystallinity of the particles. Moreover, the higher Ti K-edge absorption energy of milled ilmenite in sulfuric acid (Acid milled-I) implies the evidence of iron leaching from
iron oxide impurity, FeTiO₃ or Fe₂TiO₄ and the decrease of Fe–O–Ti linkage and/or decrease of unsaturated coordinate atom at surface layer due to high reactive with acid. By acid-assisted ball-milling, it implies the increase in active site activated sample due to the contraction in unit cell by pressure during ball milling process [30]. The feature C, D and E in the post-edge region appear at around 4984, 4992 and 5004 eV, respectively, for standard rutile TiO₂. Overall features of Ti K-edge in ilmenite ore and milled samples are closely similar to rutile TiO₂ than anatase TiO₂, accompanying the feature C, D and E appearing at lower energy than rutile TiO₂. The energy edges and post-edge peak patterns for C, D and E in ilmenite ore and prepared samples appear at lower energy from rutile TiO₂ standard reference due to iron atom correlating to Ti–O–Fe linkage that can induce the decrease in Ti atomic charge value from pure rutile TiO₂ [35, 36]. Moreover, the observable weakness of C, D, and E peak than FeTiO₃ reference indicates poor crystalline phase around Ti atom in the species of iron titanate in ilmenite ore [37]. Meanwhile, the near-edge absorption energy of Leach-AM sample indicates that the energy peak and spectra shape of C, D and E feature is close to rutile TiO₂ finger print and also pre K-edge shape, indicating high proportion of rutile TiO₂ crystalline cluster in the sample, which is unable to be measured by XRD. This result suggests that iron cluster and/or FeTiO₃ can be leached from the sample resulting to the decrease in Fe environment around Ti atom and/or increase a small fraction of FeTiO₃ crystal and TiO₂ rutile cluster. In addition, the C, D, and E of starting ilmenite ore show weak oscillation intensity pattern than standard ilmenite indicating lower crystallinity than standard ilmenite [38].

Figure 6 exhibits the Ti pre-edge region of the distorted octahedral crystal field assigned to the transition of energy from 1s to 3d transition hybridized with 4p and the 4p–4s hybridization [24, 25, 39]. The pre-edge of Ti 3d splits into the three fold t₂g state with lower energy (A) and at the higher energy of two fold e₅g orbital (B) due to the ligand field of distorted octahedral TiO₆ cluster [27]. The deconvolution of ilmenite pre K-edge reveals that local symmetry around Ti atom shows distortion of octahedral TiO₆ symmetry to tetragonal with Jahn–Teller distortion by splitting to A₁, A₂ and A₃ of peak A (t₂g) [38, 40, 41]. The high intensity of peak A2 is originated from molecular energy level contribution with Fe in Fe–Ti intervalence charge transfer via Ti–(O)–Fe linkage of face-shared octahedral [28, 32]. The deconvoluted peaks fitted with Gaussian features of pre-edge energy are depicted.
Peak A of Acid milled-I ilmenite pattern is associated to the solid residue leached by acid solution. Significant reduction of A2 peak could be explained by the leaching of iron cluster from Ti environment atom and the increase in A3 peak intensity ratio may correlated with closer lattice by ball. Ti pre K-edge absorption peak intensity of sample Leach-I and Acid milled-I exhibit observably decreasing and pre-edge shape significantly shifts toward 1s–4sp hybridization of rutile TiO2 pre-edge finger print, indicating the significant elimination of iron in ilmenite ore and increasing portion of rutile TiO2. Comparing to the rutile TiO2 standard reference, the Leach-I exhibits the combination of three-peak feature that is similar to rutile TiO2. However, the increase in A2 peak of Leach-I sample than could be due to the presence of FeTiO3 phase and small size effect of the product [38, 42, 43]. Moreover, the broadening of peak A and pre edge shape

Figure 6. (a) Ti pre K-edge energy absorption spectra; (b) Ti pre K-edge XAS peaks fitted with Gaussian feature.

Figure 7. Normalized Fe K-edge energy absorption spectra of the starting ilmenite ore, Milled-I, Acid milled-I, and Leach-I samples (a), edge energy absorption (b) and enlarge of pre K-edge spectra (c).
should be resulted from the existence of FeTiO$_3$–Ti(SO$_4$)$_2$ phase pattern occurring during leaching reaction [33]. Peak B of ilmenite ore and prepared samples located at lower energy than that of rutile TiO$_2$ should be due to the Ti–O–Fe linkage in the direction of Ti$_e$ orbital through the shared face of Ti cluster and Fe cluster which is confirmed by the existence of the ilmenite phase in sample.

Figure 7 illustrates the Fe K-edge absorption spectra of reference standards and prepared samples (figure 7(a)), the Fe K-edge XAS of ilmenite ore comparing with standard reference ((figure 7(b)) and enlargement of edge energy absorption ((figure 7(c)). Typically, Fe pre K-edge peaks and shoulder features can be interpreted as $1s \rightarrow 3d$ and $1s \rightarrow 4s$ transitions and edge adsorption feature of $1s \rightarrow 4p$ orbital. Unfortunately, the obtained pre K-edge peaks are very weak and undetectable. However, it is noticed that the $4p$ feature peak shifts toward higher energy relating to the decrease in nearest O atom neighbour distance due to high pressure at hot spot induced compress unit cell by ball milling process [29, 30]. The oxidation state and local symmetry of Fe in starting ilmenite ore and prepared samples were also investigated. The Fe K-edge absorption energies appear at 7120, 7119, 7124, and 7125 eV for Fe metal, FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$, respectively. Meanwhile, the starting ilmenite ore, Milled-I, Acid milled-I, and Leach-AM samples possess corresponding Fe K-edge energy at 7121, 7121.5, 7122, and 7125 eV, respectively. The absorption edge of ilmenite ore sample situated between FeO and Fe$_2$O$_3$ and close to FeO suggests that the ilmenite ore sample is composed of both Fe$^{2+}$ and Fe$^{3+}$ ions [34] corresponding to FeTiO$_3$ and Fe$_2$TiO$_4$ phase that is well agreeable to the XRD results. Moreover, the absorption edge of Fe$^{2+}$ (FeTiO$_3$) in ilmenite ore sample exists at higher energy than FeO as observed in figure 7(b) that may be due to the surrounding Ti$^{4+}$ ions inducing electron charge transfer via Fe–O–Ti linkage [44]. The broad peak of 1$s$-to-4$p$ transition state in the Fe XANES spectrum and also post-edge oscillation of ilmenite ore sample is attributed to the mixed of Fe$^{2+}$ and Fe$^{3+}$ in ilmenite ore sample and poor crystallinity of both clusters. This shape of transition peak feature appearing when milling in water and becomes slightly sharper when milling in sulfuric acid. This result suggests that milling process could separate iron oxide cluster from TiO$_2$ cluster accompanying decreasing Fe–O–Ti linkage or separating the amorphous part by dissolution in acid solution. Moreover, the 1$s$–to–4$p$ transition peak appears quite clearly in the Acid milled-I sample comparing to Milled-I sample advising that the amorphous phase of Fe-based oxide can be lessened by milling process with sulfuric acid. Besides, the scattering feature in peak shape of Leach-AM tend to approach to Fe$_3$O$_4$ pattern intimating that the greater content of Fe$^{3+}$ cluster than Fe$^{2+}$ cluster. Comparing to Fe$_3$O$_4$ reference, Fe K-edge absorption spectrum of the Acid-milled-I sample slightly moves to higher energy with the increase in oxidation state close to oxidation state of +3, which is corresponding to more compress unit cell according to result from XRD (figure 4(b)). This result suggests that probable contribution of Fe$^{2+}$ ions in the sample and FeTiO$_3$ phase can be diminished by acid-assisted mechanical leaching process rather than Fe$_2$TiO$_4$ phase.

4. Conclusion

The main phases of ilmenite ore consist of FeTiO$_3$, Fe$_2$TiO$_4$ and small amount second phases of rutile TiO$_2$ and Fe$_2$TiO$_5$ confirmed by XRD pattern. The crystallite size of milled ilmenite powder in acid-assisted ball-milling was distinctly decreased comparing to the sample milled with DI water according to XRD result and TEM images. For XAS spectra of activated ilmenite nanopowders, the distortion of TiO$_6$ octahedral cluster and XRD spectra showing amorphousity in ilmenite ore tends to occur by milling process. The acid-assisted mechanical ball-milling process could also induce high active surface of distortion of TiO$_6$ octahedral and/or unsaturated coordination Ti atom at surface without sulphate salts of TiOSO$_4$ or FeSO$_4$. In addition, this acid-assisted ball-milling technique also seems to be good method for iron leaching during milling activation process. These results imply that iron compound can be eliminated by mechanical ball-milling assisted by acid solution.

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