Article

Fabrication of Adsorbed Fe(III) and Structurally Doped Fe(III) in Montmorillonite/TiO₂ Composite for Photocatalytic Degradation of Phenol

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Abstract: The Fe(III)-doped montmorillonite (Mt)/TiO₂ composites were fabricated by adding Fe(III) during or after the aging of TiO₂/Ti(OH)₄ sol-gel in Mt, named as $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ and Fe/Mt/TiO_2 , respectively. In the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$, Fe(III) cations were expected to be located in the structure of TiO₂, in the Mt, and in the interface between them, while Fe(III) ions are physically adsorbed on the surfaces of the composites in the Fe/Mt/TiO_2 . The narrower energy bandgap (E_g) lower photo-luminescence intensity were observed for the composites compared with TiO₂. Better photocatalytic performance for phenol degradation was observed in the Fe/Mt/TiO_2 . The 94.6% phenol degradation was due to greater charge generation and migration capacity, which was confirmed by photocurrent measurements and electrochemical impedance spectroscopy (EIS). The results of the energy-resolved distribution of electron traps (ERDT) suggested that the Fe/Mt/TiO_2 possessed a larger amorphous rutile phase content in direct contact with crystal anatase than that of the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. This component is the fraction that is mainly responsible for the photocatalytic phenol degradation by the composites. As for the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$, the active rutile phase was followed by isolated amorphous phases which had larger (E_g) and which did not act as a photocatalyst. Thus, the physically adsorbed Fe(III) enhanced light adsorption and avoided charge recombination, resulting in improved photocatalytic performance. The mechanism of the photocatalytic reaction with the Fe(III)-doped Mt/TiO₂ composite was proposed.

Citation: Zhang, L.; Chuaicham, C.; Balakumar, V.; Ohtani, B.; Sasaki, K. Fabrication of Adsorbed Fe(III) and Structurally Doped Fe(III) in Montmorillonite/TiO₂ Composite for Photocatalytic Degradation of Phenol. *Minerals* **2021**, *11*, 1381. <https://doi.org/10.3390/min11121381>

Academic Editor: Andrey G. Kalinichev

Keywords: montmorillonite; Fe(III); TiO₂; photocatalysis

Received: 8 November 2021

Accepted: 4 December 2021

Published: 8 December 2021

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1. Introduction

Mt and Fe(III) are abundant in nature, while Ti is one of the most abundant elements (the ninth most abundant element (0.63% by mass)), and the seventh most abundant metal in Earth's crust. Ti can be found in almost all living things, as well as in bodies of water, rocks, and soils. The most common compound is titanium dioxide (TiO₂), a popular photocatalyst that has long been studied and applied to scientific research and industry. TiO₂ is highly photocatalytic-active, non-toxic, chemically stable in most conditions, and has a low cost. However, the relatively large energy bandgap (E_g) and the recombination of electron (e^-) and hole (h^+) reduce the photocatalytic activity of TiO₂. In addition, the nanoparticles of TiO₂ tend to aggregate, making it difficult to separate from water. To overcome these difficulties, numerous strategies have been applied, such as morphology modification [1,2], surface sensitization [3,4], metal nanoparticle deposition [5,6], element doping [7,8], and the preparation of composite materials with other materials [9,10].

Montmorillonite (Mt) is a typical supporting material to make composites with TiO₂ to avoid aggregations of TiO₂ particles, because the TiO₂ particle sizes were reduced and had a better distribution in the Mt layers. Moreover, the significantly reduced fine particle sizes can improve the photocatalytic performance of TiO₂ [11–13]. Mt is a 2:1 clay mineral,

with a layered structure and exchangeable interlayer cations [14–16], which is sufficiently distributed in nature [16,17]. Consequently, Mt has excellent adsorption abilities, especially for positively charged substances with large relative surface areas. Besides this, Mt is relatively stable in a wide range of pHs. All of these properties make Mt a good supporting material to prepare composites [18–20]. However, it does not have any photocatalytic properties due to a large bandgap [21]. Iron is the fourth most abundant element in that layer. Moreover, iron species are one of the least toxic and least expensive substances that are photocatalytic in the visible region of the spectrum. However, the trace amounts of iron in natural minerals have been ignored. Many studies have suggested that iron doping in materials can give or facilitate the photocatalytic property of materials. In the layered double hydroxide (LDH) (or other clay) containing Fe(III)/Fe(II), a non-negligible promoting effect has been achieved in photocatalytic reactions [22–24]. Using density functional theory (DFT) calculation, a middle-gap electron trap state has been generated in the case of iron doping, thus improving the photocatalytic efficiency of the ZnTi-LDH/clay samples [25]. However, these studies did not discuss whether the Fe(III) was in the form of cation, metal oxide, metal hydroxide, or other forms. Moreover, the location of the Fe(III) in the composite was obscure.

Numerous studies have been applied on the Fe(III) doping of TiO₂ since the Fe(III) ion in TiO₂ can introduce a Fermi level as an electron donor or acceptor, narrowing the E_g of the TiO₂ and red shifting the irradiation adsorption of TiO₂ [26–28]. It was also vigorously proposed that the metal undergoing transition with TiO₂ generates oxygen vacancies, which act as the charge trapping sites promoting the generation of active radicals [29,30].

To better understand the role of clay and iron in such types of composites, two types of Mt-TiO₂ composites with Fe(III) doping materials were synthesized and applied to the phenol degradation. Environmental pollution and destruction on a global scale is a growing concern today [31–33]. Refractory organics with aromatic structures are one of the most threatening contaminants that are toxic to human beings, microorganisms, animals, plants, and ecosystems [34,35]. There is an urgent requirement for the remediation of organic pollutants. Phenol contains one aromatic ring and one oxhydroxyl group. Phenolic compounds are ubiquitous and toxic in low concentrations [36]. More importantly, with phenol kept neutrally charged under pH 10 [37], the adsorption or repulsion from Mt can be prevented. Therefore, detecting the photocatalytic degradation of the materials in phenol can give clues about their photocatalytic capacity towards other organics.

In this paper, the distribution of Fe(III) on the Mt/TiO₂ composites was controlled by changing the timing of when Fe(III) was added to the composites. Thus, the role of Fe(III) can be revealed based on its location in the composites. The whole synthesizing procedure was strictly controlled under pH 2 to inhibit any form of iron oxides or iron hydroxides. The Fe(III) should be always in the form of the cation. We have described the procedure for the preparation of Fe/Mt/TiO₂, where Fe(III) was adsorbed in the surface of the composites, and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$, where Fe(III) was doped in the structure of the TiO₂ in the composites. These two Fe(III)-doped Mt/TiO₂ composites were applied for photocatalytic degradation of phenol. The photocatalytic mechanism for phenol degradation using the composites was proposed.

2. Materials and Methods

2.1. Materials

Na-Mt (Kunipia-F) with a cation exchange capacity (CEC) of 1.114 mmol/g (Bergaya and Vayer, 1997) was bought from Kunimine Industries Co. Ltd. (Tokyo, Japan). Through an elemental analysis (method of ME-ICP61, ALS Global Ltd., North Vancouver, Canada), the chemical formula of Kumipia-F is given by $(\text{Na}_{0.97}\text{Ca}_{0.08})^{+1.13}(\text{Si}_{7.68}\text{Al}_{0.32})(\text{Al}_{2.94}\text{Fe}^{\text{III}}_{0.25}\text{Fe}^{\text{II}}_{0.03}\text{Mg}_{0.78})\text{O}_{20}(\text{OH})_4^{-1.13}\cdot n\text{H}_2\text{O}$. Iron(III) nitrate enneahydrate ($\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, 99%), iron(III) chloride (FeCl_3 , 95%), sodium hydroxide (NaOH , 97.0+%), hydrochloric acid (HCl , 1.17), and nitric acid (HNO_3 , 1.38) were acquired from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Titanium(IV) chloride (TiCl_4 , 99%)

and Millipore water with pH 6.31 were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan) and Synergy UV (Merck, Darmstadt, Germany), respectively.

2.2. Preparation of Iron-Modified Mt and Clay/TiO₂ Composites

To synthesize protonated Mt (H-Mt) and Fe(III)-doped Mt (Fe-Mt), Mt was added to HNO₃ or Fe(III) (Fe(NO₃)₃·9H₂O, 99%) solution which has a pH of 2 and was vigorously stirred at room temperature for 1 h (S/L = 10 g/L). Next, the H-Mt and Fe-Mt were centrifuged, rinsed, collected, lyophilized, ground, and sieved (<149 μm). Leveraging the sol-gel technique, Ti(OH)₄/TiO₂ nanoparticles were generated in aqueous media, following which TiCl₄ and HCl were then added to Milli-Q water. The resultant solution contained 0.83 M TiCl₄ and 1.0 M HCl, which was further stirred for 1 h and left to stand still for 6 h. Through hydrolysis, a nearly transparent, stable Ti(OH)₄/TiO₂ sol-gel was attained.

Before heterocoagulation, the acidity of Ti(OH)₄/TiO₂ sol was altered to pH = 2 with the addition of a NaOH solution since it has an original pH value of around 0. Next, the Sol-gel was added to 1% (g clay/100 mL of water) H-Mt suspension. Meanwhile, the Fe(III) eqv. to 0.274 mmol/g Mt was added for $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ samples exclusively. Both kinds of samples were vigorously stirred for 30 min. The theoretical concentration of TiO₂ would be 30% (m/m). Heterocoagulated Fe/Mt/Ti(OH)₄-TiO₂ (Fe/Mt/TiO₂) or $x\text{Fe-Mt}/(1-x)\text{Fe-Ti(OH)}_4\text{-TiO}_2$ ($x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$) precipitated after 20 h of sedimentation at 70 °C, 80 °C, and 90 °C. Fe(III) was added for Fe/Mt/TiO₂ samples immediately after sedimentation. All the suspensions were stirred for another 1 h, followed by centrifugation at 8300 rpm for 30 min. The obtained solid substance was rinsed with Milli-Q water, freeze-dried for 24 h, ground, and sieved (<149 μm). Residual Fe(III) in the supernatant was detected by the inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer 8500, Waltham, MA, USA). The samples synthesized at 70 °C were the main focus for comparison because the synthesis temperature did not influence the photocatalytic performance of the Fe/Mt/TiO₂ composites (Figure S1).

2.3. Solid Characterization

The resultant composites were inspected with X-ray fluorescence (XRF, Shimadzu-EDX800, Kyoto, Japan). Powder X-ray diffraction (XRD) patterns of materials were recorded with an Ultima IV X-ray diffractometer (Rigaku, Akishima, Japan) by Cu Kα radiation produced at 40 kV and 40 mA, a divergence slit of 1.0 mm, an anti-scatter slit of 10 mm, and a receiving slit of 0.15 mm over a 2θ of 2.0–10°, with a step size of 0.02° and a scanning speed of 2°/min. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCA 5800 system (Ulvac-PHI, Kanagawa, Japan) with a monochromatic Al Kα X-ray source at 200 W. A survey scan was carried out from 0 to 1000 eV with passing energy of 187.85 eV, narrow scans of N 1 s, as well as C 1 s orbitals, which were acquired using passing energies of 23.5 and 58.7 eV. Peak separation was performed with Casa XPS software (Version 2.3.16 PR 1.6) following the subtraction of a Shirley baseline. Binding energies (EB) of peaks were calibrated using EB [C 1s] = 284.6 eV. The scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) investigations were performed on a VE-9800 scanning electron microscope (Keyence, Osaka, Japan) with an accelerating voltage of 20 kV. The transmission electron microscopy (TEM) and EDX were applied using a JEM-2100HCKM, JEOL (Akishima, Japan). Diffuse reflectance spectroscopy (DRS) was conducted with a range of 200–800 nm on a UV-2450 spectrophotometer which has a diffuse-reflectance attachment with BaSO₄ as a reference. Solid-state photoluminescence spectroscopy (PL) was conducted with a JASCO F-6600 spectrofluorometer. Electrochemical properties, such as photocurrent response and the electrochemical impedance spectroscopy (EIS) of composites, were examined by the 1280c AMETEK advanced measurement technology (Berkshire, United Kingdom). Later, 200 mg of Fe/Mt/TiO₂ and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ composites were included in a periodic acid-Schiff (PAS) cell which contained an electret condenser microphone and a quartz window on top under N₂ flow saturated with methanol vapor

for a minimum of 30 min. The light beam from a Xe lamp with a grating monochromator modulated at 80 Hz using a light chopper was emitted in the range of 650 nm–350 nm through the cell window to identify the PAS signal with a digital lock-in amplifier. The energy-resolved distribution of electron traps (ERDT) was obtained by figuring out the amount of photo absorption change for the accumulated electrons.

2.4. Photocatalytic Activity Test

The photocatalytic activities of synthesized products were tested for phenol degradation under the irradiation of a 300 W xenon lamp. Before the irradiation, 20 mg of the photocatalyst was suspended in 100 mL of 10 mg/L phenol aqueous solution in a photoreactor with a cooling water jacket outside. The suspensions were stirred at 500 rpm in darkness for 5 min to arrive at an adsorption–desorption equilibrium. In the irradiation process, approximately 1 mL of suspension was collected from the reaction cell at proper intervals and was subsequently filtered by a 0.45- μ m cellulose acetate membrane filter for removal of the photocatalyst. Afterward, the solutions were examined by high-performance liquid chromatography (HPLC) [38]. The concentrations of phenol, together with its degradation products, were estimated by evaluating the absorption of these substances at a wavelength of 270 nm. Scavenger tests and the reusability test were carried out following the aforementioned procedures. For the scavenger test, 50 mmol of ethanol, isopropanol, and para-benzoquinone was added before the addition of photocatalytic materials.

3. Results

3.1. Characterizations

After the filtration of the synthesized Fe/Mt/TiO₂ and x Fe-Mt/(1 – x)Fe-TiO₂, the remaining Fe(III) was detected by ICP-OES. The Fe(III) concentration was below the detection limit of the ICP, suggesting that almost all the added Fe(III) was doped in the composites. Therefore, the doped amount of Fe(III) in all the composites were the same and should not be the impact factor influencing the photocatalytic character of the samples. XRF was applied to calculate the weight percentage of the TiO₂ phase in the whole composite (Table 1). When comparing the Fe/Mt/TiO₂ and x Fe-Mt/(1 – x)Fe-TiO₂, the Fe/Mt/TiO₂ always kept a slightly higher amount of TiO₂ than x Fe-Mt/(1 – x)Fe-TiO₂, but the difference was not significant. The highest TiO₂ content was obtained when the product was synthesized at 80 °C. When compared with clay/TiO₂ composites synthesis without Fe(III) in previous research [39–41], the optimal temperature for the highest TiO₂ yield was at 70 °C. The presence of Fe(III) in composites required a higher synthetic temperature for the highest TiO₂ yield.

Table 1. Elemental composition of Fe/Mt/TiO₂ and x Fe-Mt/(1 – x)Fe-TiO₂ with different synthesis temperatures (70 °C, 80 °C, and 90 °C) in wt%.

T (°C)	Sample	Na (%)	Mg (%)	Al (%)	Si (%)	Ca (%)	Ti (%)	Fe (%)	TiO ₂ (%)
90	Fe/Mt/TiO ₂	N.D.	1.84	11.78	31.08	0.05	50.07	5.19	27.63
	x Fe-Mt/(1 – x)Fe-TiO ₂	N.D.	1.97	12.28	32.28	0.05	47.49	5.92	26.74
80	Fe/Mt/TiO ₂	N.D.	1.86	11.65	30.74	0.04	49.62	6.10	27.65
	x Fe-Mt/(1 – x)Fe-TiO ₂	N.D.	1.86	11.80	30.54	0.07	48.80	6.94	27.50
70	Fe/Mt/TiO ₂	N.D.	1.88	12.29	32.29	0.03	48.23	5.28	26.91
	x Fe-Mt/(1 – x)Fe-TiO ₂	N.D.	1.88	12.04	32.14	0.08	47.19	6.66	26.77

The XRD patterns of the original Mt, Fe(III) cation-doped Mt (Fe-Mt, synthesized at ambient temperature), TiO₂, Fe/Mt/TiO₂, and x Fe-Mt/(1 – x)Fe-TiO₂ synthesized at 70 °C were analyzed, and the XRD pattern of these samples was shown in Figure 1. The 001 peaks from Mt included the interlayer distance and the thickness of one layer (0.96 nm) [42]. The interlayer distances in the Fe-Mt, Fe/Mt/TiO₂, and x Fe-Mt/(1 – x)Fe-TiO₂ were almost the same value (0.42/0.43 nm) when compared with the original Mt (0.25 nm), which suggested

that only ion exchange of Fe(III) with the interlayer cations in Mt occurred during the synthesis of the composites. Additionally, the TiO_2 should only be distributed on the surface of Mt. The hydrated ionic sizes of Fe(III) are 0.45 nm [42]. The smaller interlayer distances of the Mt in the composites, rather than the ionic sizes, may be distributed from the Van der Waals force among the aluminosilicate layers extruding from the hydrated shell of Fe(III), which are imperfectly shaped [42].

Figure 1. XRD patterns of original Mt, Fe-Mt synthesized at RT, TiO_2 , Fe/Mt/ TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ synthesized at 70 °C.

The only single anatase phase of TiO_2 was presented for the pristine TiO_2 . For both Fe/Mt/ TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$, the 101 and 004 peaks at 25.4 and 37.9° (JCPDS No. 21-1272) of anatase phase were detected. Additionally, the 110 peak of rutile was formed at 28.3°. The representative 001, 003, and 101 reflection peaks of Mt in the composites were detected at 6.0–6.5, 19.8, and 35.2°, respectively [43]. The formation of TiO_2 in the composites by different synthetic temperatures was elucidated, and their XRD patterns were presented in Figure S2. Peak separation was utilized to further analyze the XRD patterns in more detail in Figure 2. The typical 101 diffraction of anatase at 25.4° and the 110 diffraction of rutile between 28.2–28.4° were well fitted. The parameters after peak fitting were listed in Table S1. The large full width at half-maximum (FWHM) values for anatase and rutile related to the broad peaks of all the samples suggested a low crystallinity of the TiO_2 phase on the Mt layers. The TiO_2 content in $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ at three synthesized temperatures was higher than in Fe/Mt/ TiO_2 , and the Fe(III) in TiO_2 can improve the crystallization of the anatase phase. Increasing the temperature can improve the crystallization of anatase in Fe/Mt/ TiO_2 but depress it in $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ from 80 °C to 90 °C. As proven by ICP analysis, only the location of Fe(III) can dominate the growth of TiO_2 phases on the aluminosilicate layers of Mt. For the following characterizations, the Fe/Mt/ TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ synthesized at 70 °C were applied to compare with previous studies.

Figure 2. Peak fitting of the XRD patterns ($20\text{--}35^\circ$ in 2θ) of Fe/Mt/TiO₂ and xFe-Mt/(1 − x)Fe-TiO₂ with different synthesis temperatures (70, 80, and 90 °C). Peaks in blue were from anatase and peaks in yellow were from rutile.

The morphology of the TiO₂, Fe/Mt/TiO₂, and xFe-Mt/(1 − x)Fe-TiO₂ composites in μm scale was investigated by the SEM observation (Figure 3). The TiO₂ particle sizes were significantly reduced in the Mt layer in the Fe/Mt/TiO₂ and xFe-Mt/(1 − x)Fe-TiO₂ composites; furthermore, the Mt stacking layers in Fe/Mt/TiO₂ and xFe-Mt/(1 − x)Fe-TiO₂ were even smaller than in the pure TiO₂. From the SEM-EDX for both the Fe/Mt/TiO₂ (Figure 3d–i) and xFe-Mt/(1 − x)Fe-TiO₂ (Figure 3j–o), the TiO₂ nanoparticles intensively covered the surface of the Mt particles. The TiO₂ covering of the Mt layers in Fe/Mt/TiO₂ in the nanometer scale was further observed through TEM-EDX, as illustrated in Figure 4. A higher intensity of Al distribution was observed in the Ti-empty/-lacking regions, which indicated the overlapping of TiO₂ particles in the Mt layers. The low-intensity distribution of Al in the Ti-concentrated region should be attributed to the occluding of TiO₂. The even distribution of Fe elements suggested the relative homogeneous distribution of Fe(III) on all of the Mt phase, TiO₂ phase, and in the interface between the Mt and TiO₂.

The electronic level and chemical composition of Fe/Mt/TiO₂ and xFe-Mt/(1 − x)Fe-TiO₂ were investigated by XPS and depicted in Figures S3 and S4. In the wide-scan spectrum for the Fe/Mt/TiO₂ and xFe-Mt/(1 − x)Fe-TiO₂ (Figures S3a and S4a), the dominant peaks attributed to the Ti 2p orbitals were raised from TiO₂, and the dominant peaks attributed to the O 1s, Si 2p, and Al 2p orbitals were raised from Mt. The deconvolution peaks from the Ti 2p orbitals represented two peaks for both the Fe/Mt/TiO₂ and xFe-Mt/(1 − x)Fe-TiO₂ in Figures S3b and S4b. The peaks at 464.3–464.4 and 458.7 eV were attributed to the Ti (IV) 2p_{1/2} and 2p_{3/2} orbitals [44]. The deconvoluted spectra of Fe 2p (Figures S3c and S4c) for both composites showed two peaks that are assigned to Fe(III) 2p_{1/2} and 2p_{3/2} at 723.9–725.5 and 713.2–713.4 eV, respectively [45]. In the C 1s region of the Fe/Mt/TiO₂ and the xFe-Mt/(1 − x)Fe-TiO₂ (Figures S3d and S4d), the peaks at 288.6–289.0, 286.3–287.0, and 284.6 eV are from C = O, C—O, and C—C, respectively [46]. In the O 1s region of the Fe/Mt/TiO₂ and xFe-Mt/(1 − x)Fe-TiO₂ (Figures S3e and S4e), the peaks at 533.0–534.3, 531.7–531.9, and 530.1–531.0 eV are from absorbed H₂O on the surface, hydroxide bonds, and oxide bonds, respectively [47–49]. The peak raised at 102.5 in both composites, as is shown in Figures S3f and S4f, are both assigned to tetrahedral

Si—O [50,51]. The valence band (VB) on top of the Fe/Mt/TiO₂ and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ was estimated by drawing the straight tangent line to the VB spectrum of the samples in Figure 5 [52,53], and the values are 1.72 and 1.95 eV, respectively.

Figure 3. SEM images of: (a) TiO₂; (b) Fe/Mt/TiO₂; and (c) $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. SEM-EDX K α maps of: (d) titanium; (e) iron; (f) silica; (g) aluminum; (h) magnesium; and (i) oxygen for Fe/Mt/TiO₂. SEM-EDX K α maps of: (j) titanium; (k) iron; (l) silica; (m) aluminum; (n) magnesium; and (o) oxygen for $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. Scale bars were adjusted to be the same and indicate 50.00 μm .

Figure 4. Images of: (a) TEM-EDX, (b) TEM images, and K α maps of: (c) titanium; (d) aluminum; and (e) iron for Fe/Mt/TiO₂.

Figure 5. XPS valence band (VB) energy region of: (a) Fe/Mt/TiO₂; (b) xFe-Mt/(1 − x)Fe-TiO₂.

3.2. Investigation of Optical and Charge Separation Properties

As indicated by the UV-DRS spectra of the TiO₂, Fe/Mt/TiO₂, and xFe-Mt/(1 − x)Fe-TiO₂ (Figure 6a), it can be determined that both composites exhibited higher absorbance in the visible light region compared to pure TiO₂ due to the additional Mt and Fe(III) in the composites. Compared to Fe/Mt/TiO₂, the xFe-Mt/(1 − x)Fe-TiO₂ composite showed a slight red shift in the absorption edge, and such an extension in the absorption band influenced the optical properties of samples significantly. By using the Tauc plotting Kubelka–Munk function versus energy, the optical bandgap energy (E_g) of Fe-Mt can be evaluated, according to Equation (1) (Figure 6b) [54–56]:

$$\alpha h\nu = k(h\nu - E_g)^{n/2} \quad (1)$$

where α , h , ν , k , and E_g denote the absorption coefficient, Planck constant, light frequency, proportionality constant, and bandgap energy, respectively. The value of n is dependent on the type of optical transition of the measured semiconductor (for direct transition, $n = 1$; for indirect transition, $n = 4$ [57]). For TiO₂, Fe/Mt/TiO₂, and xFe-Mt/(1 − x) Fe-TiO₂, the calculated bandgap values of samples were estimated to be approximately 3.24, 3.24, and 3.19 eV, respectively (Figure 6b). The lower E_g of the xFe-Mt/(1 − x)Fe-TiO₂ may be due to the generation of a new electronic level of Fe(III) in the structure of the TiO₂ [58,59].

Figure 6. (a) DRS-UV spectra; (b) corresponding Tauc plots of Fe/Mt/TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ synthesized at 70 °C.

The recombination rate of e^- - h^+ pairs was measured using PL (Figure 7). The higher PL intensity of TiO_2 compared to the other two composites suggested that the better charge separation efficiency on the composite was mainly due to the effects of Mt. In comparison with the Fe/Mt/TiO_2 , $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ showed a decreased luminous intensity, which may be because the doped Fe(III) in the structure of the TiO_2 generated the middle-gap state to avoid the recombination of the e^- - h^+ pairs in the TiO_2 .

Figure 7. Photoluminescence of Fe/Mt/TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ at 70 °C.

Furthermore, with the transient photocurrent response measurements and EIS to relate with the photocatalytic phenol degradation activity, the transfer and production of electrons in the TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ were investigated. As exhibited in Figure 8a,

the photocurrent density was ranked as $\text{Fe/Mt/TiO}_2 > x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2 > \text{TiO}_2$. Moreover, the EIS spectra of the TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ were measured, as shown in Figure 8b. According to the results, a smaller radius of the EIS Nyquist diagram was discovered in the Fe/Mt/TiO_2 , which suggested a lower charge transfer resistance to improve the photocatalytic activity.

Figure 8. (a) Photocurrent density versus time measurements of Mt, Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ synthesized at 70 °C under 0 V versus Ag/AgCl bias; (b) Nyquist plots of the EIS spectra of Mt, Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ synthesized at 70 °C.

3.3. Photocatalytic Activity

Figure 9a presents the photocatalytic removal of phenol as a function of reaction time using the TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. In the dark conditions, a slight adsorption of phenol was observed for all the samples. On the other hand, the adsorption reached equilibrium within the first 5 min, and it predominantly occurred on the surface of the samples via physical adsorption. In comparison, the Fe/Mt/TiO_2 showed the highest photocatalytic performance of 94.6% on phenol degradation for 3 h. The adsorbed Fe(III) on the surface of the composite and the interlayer of Mt can improve the photocatalytic activity. Photocatalytic reduction kinetics of phenol fitted well to pseudo-first-order kinetics (Equation (2)) (Figure 9b) [60]:

$$-\ln(C/C_0) = kt \quad (2)$$

where C and C_0 (mmol/g) refer to the residual and initial concentrations of phenol and parameter k (min^{-1}) marks the rate constant of the pseudo-first-order model. The parameters for the pseudo-first-order were listed in Table S1. The correlation coefficient (R^2) for the pseudo-first-order is more than 0.980 for all three samples, and the chi-square for all the samples is of -4 order of magnitude. Therefore, the pseudo-first-order model can predict kinetics. The rate constants are 0.015, 0.022, and 0.037 min^{-1} for the TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$, respectively. The Fe/Mt/TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ showed superb efficiency. Most importantly, the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ had a higher capacity than the Fe/Mt/TiO_2 , which is consistent with the photocurrent, but the impedes the results and goes against the DRS and PL results.

Figure 9. (a) Photocatalytic degradation and (b) kinetics of phenol by TiO_2 , Fe/Mt/TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ composites synthesized at 70°C .

The reusability test was applied (Figure 10) to investigate the chemical stability of the Fe/Mt/TiO_2 , which possessed the better photocatalytic performance during the photocatalytic oxidation of phenol. High photocatalytic degradation of phenol in the Fe/Mt/TiO_2 was maintained over 93.1% for three cycles. The slight reduction of the photocatalytic performance after the first cycle should be due to the mass loss of the samples during washing.

Figure 10. Reusability test of Fe/Mt/TiO_2 synthesized at 70°C for phenol degradation.

3.4. ERDT Patterns of TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$

Reversed double-beam photoacoustic spectroscopy (RDB-PAS) was utilized to investigate the surface electronic properties of Fe-Mt, TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. The obtained ERDT could indicate the surface photocatalytic properties of the measured samples [61]. Figure 11 shows the ERDT patterns for Fe-Mt, TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$, and the parameters are listed in Table 2. This technique can be applied only to n-type semiconductors; thus, Fe-Mt had no electron trap (ETs) on ERDT because Fe(III) generated a Fermi level as an electron donor which is a p-type characteristic of semiconductor. The energy-reversed distribution of electron traps emerged at energy ranges of 2.20–4.00 eV for the TiO_2 , Fe/Mt/TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. This suggested that there were TiO_2 phases covering the surfaces of the composites. The electron trapping patterns of TiO_2 were fitting using peak separation. Three peaks at 2.96, 3.22, and 3.44 eV were assigned as crystal rutile, amorphous rutile, and amorphous rutile covered with crystal anatase, respectively. The dominance of the amorphous phase was consistent with the low crystallinity of the TiO_2 which was suggested in XRD results (Figure 2 and Table S1). The ERDT patterns of the Fe/Mt/TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ were also separated. The peak at 3.44 eV represents the amorphous rutile covered in crystal anatase which also emerged in the pattern of the TiO_2 . Crystal TiO_2 should be the dominant fraction for photocatalytic reaction, and the amorphous phase may gain the photocatalytic activity the presence of crystal phase in the TiO_2 [62–64]. The crystal anatase in both composites was covered by amorphous TiO_2 . Only the amorphous TiO_2 directly in contact with the crystal phase should be responsible for photocatalytic activity. The intensity of this kind of rutile peak in the Fe/Mt/TiO_2 (85.4%) was twice of that in the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ (43.5%). Therefore, this result can explain why the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ showed lower photocatalytic activity for the degradation of phenol than the Fe/Mt/TiO_2 . Both electron accumulation peaks at 3.62 and 3.76 eV were attributed to isolated amorphous TiO_2 that will be not in contact with the crystal phase of the TiO_2 . This fraction of the TiO_2 on the composite was expected to have negligible photocatalytic activity. Besides, the total intensity of the isolated TiO_2 phase on the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ was much higher than on the Fe/Mt/TiO_2 and may overlap with the photocatalytic active amorphous rutile, depressing the charge generating and transferring.

Table 2. Parameters of ERDT peak fitting of Fe/Mt/TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. c-R, a-R, a-R on c-A, and iso- TiO_2 are the abbreviation of crystal rutile, amorphous rutile, amorphous rutile covered on crystal anatase, and isolated amorphous TiO_2 , respectively.

Sample	Peak Assignment	Peak Position (eV)	Relative Intensity (%)
TiO_2	c-R	2.96	31.1%
	a-R	3.22	42.0%
	a-R on c-A	3.44	27.0%
	iso- TiO_2	3.62	N.D.
	iso- TiO_2	3.76	N.D.
Fe/Mt/TiO_2	c-R	2.96	N.D.
	a-R	3.22	N.D.
	a-R on c-A	3.44	43.5%
	iso- TiO_2	3.62	52.2%
	iso- TiO_2	3.76	4.3%
$x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$	c-R	2.96	N.D.
	a-R	3.22	N.D.
	a-R on c-A	3.44	85.4%
	iso- TiO_2	3.62	N.D.
	iso- TiO_2	3.76	14.6%

Figure 11. Peak separation of the representative energy-resolved distribution of electron traps (ERDTs) patterns of Fe-Mt synthesized at RT, and TiO_2 , Fe/Mt/ TiO_2 , and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ synthesized at 70°C plotted as a function of energy (eV) from the valence band top (VBT) combined with CBB. The numbers in brackets denote the relative total electron trap density. Peaks at 2.96, 3.22, 3.44, and 3.62–3.76 eV were assigned as crystal rutile, amorphous rutile, amorphous rutile covered on crystal anatase, and isolated amorphous TiO_2 .

3.5. Radical Scavenger Tests

During the progress of the light irradiation, the radicals generated are responsible for the photocatalytic reaction. To detect which radical can be predominantly generated throughout the photocatalytic reaction, radical scavengers were added during the photocatalytic degradation of phenol in the Fe/Mt/ TiO_2 , which is the best photocatalyst (Figure 12). Ethanol is the h^+ scavenger, and isopropanol is the $\cdot\text{OH}^-$ scavenger. The addition of both ethanol and isopropanol had a slight impact on the photocatalytic performance of the Fe/Mt/ TiO_2 , with a rate constant of 0.014 for both. It means that the h^+ and $\cdot\text{OH}^-$ should not be the main radical sources for the photocatalytic reaction. A significant depression for the photocatalytic degradation of phenol with the rate constant of 0.010 was observed with the addition of para-benzoquinone, which is the $\cdot\text{O}_2^-$ radical scavenger. Therefore, $\cdot\text{O}_2^-$ is the dominant radical for the photocatalytic degradation of phenol. This phenomenon is reasonable because the VB calculated from XPS results was higher than the reduction potential of the $\cdot\text{OH}^-$ production. Thus, the $\cdot\text{OH}^-$ radical should not be directly generated by the Fe/Mt/ TiO_2 .

3.6. Photocatalytic Mechanisms

Based on the above results, the mechanisms of both the Fe/Mt/ TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ could be proposed (Scheme 1). In both composites, the crystal anatase will not be directly exposed on the surface but in contact with the amorphous rutile, which is performed as the main photocatalyst. The amount of amorphous rutile covered in crystal anatase in the Fe/Mt/ TiO_2 was approximately twice that in the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. On the contrary, the amount of isolated amorphous anatase and rutile overlapping with the photocatalytic active sites in $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ was much higher. These two factors resulted in a higher photocatalytic activity for the Fe/Mt/ TiO_2 than the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$. Based on DRS and E_g results, the TiO_2 phase in the Fe/Mt/ TiO_2 has an E_g of 3.24 eV, with the 1.75 eV energy level of VB and the 1.49 eV energy level of CB. Additionally, the TiO_2 phase in the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ has an E_g of 3.19 eV, with the 1.95 eV energy level of VB and -1.24 eV energy level of CB. The VBT of both the Fe/Mt/ TiO_2 and the

$x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ are lower than the reduction potential of $\cdot\text{OH}^-$ production [25]. So, the h^+ and OH^- should have little influence on the photocatalytic degradation of phenol. In addition, the radical scavenger test for the Fe/Mt/TiO_2 also proved that the O_2^- should be the predominant radical during the photocatalytic reaction. The Fe(III) located on the interlayer and surface of the Mt in both composites may generate a new Fermi level [25] and establish heterojunctions with the bulk TiO_2 in the composites to reduce the charge recombination and enhance electron transfer.

Figure 12. Effects of radical scavengers (ethanol, isopropanol, and para-benzoquinone) on the photocatalytic degradation of phenol in the Fe/Mt/TiO_2 composite synthesized at 70°C . Isopropanol is the $\cdot\text{OH}^-$ scavenger, ethanol is the h^+ scavenger, and para-benzoquinone is the O_2^- scavenger.

Scheme 1. The band edge positions of Fe/Mt/TiO_2 and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ with respect to standard hydrogen electrode (SHE), where the $E(\text{vs. SHE}) = -(E(\text{vs. vacuum}) - 4.44)\text{ V}$.

4. Conclusions

The Fe/Mt/TiO₂ was prepared by introducing Fe(III) cations into the Mt/TiO₂ composite after the formation of the Mt/TiO₂ composite, while the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ was obtained by the doping of Fe(III) cations during the formation of the Mt/TiO₂ composite. The locations of the Fe(III) cations in the Fe/Mt/TiO₂ were expected to be on the surface of the composite and in the interlayers of the Mt, while the Fe(III) cations in the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ may exist in the structures of TiO₂ and Mt. The different locations of the doped Fe(III) in the composite directly interferes with the formation of the TiO₂ content in the composite. The wt% of the TiO₂ in the Fe/Mt/TiO₂ always kept higher (26.91–27.63%) than in the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ (26.77–27.50%), but the anatase to rutile ratio was always lower (0.92–1.45 for Fe/Mt/TiO₂ and 1.53–1.91 for $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$). Both composites' optical and electrochemical properties and photocatalytic phenol degradation activity were better than that of pristine TiO₂, due to the formation of the heterojunction between TiO₂ and Mt, and the introduction of Fe(III) into the composites. Compared between two composite samples, the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ composite showed better light absorption abilities (*E_g*: 3.19 eV) than the Fe/Mt/TiO₂ composite (*E_g*: 3.24 eV), confirmed by DRS results because the doped Fe(III) in the structure of the TiO₂ generates a new electronic level to reduce the *E_g*. However, the Fe/Mt/TiO₂ exhibited a better charge generation ability, which was proven by the higher peak intensity in the photocurrent and a smaller radius in the EIS. The photocatalytic degradation of phenol was 94.6% for the Fe/Mt/TiO₂, which was higher than that of the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ at 85.1%. These are due to the higher active fractions of amorphous rutile covered in crystal anatase on the surface of the composite (two-times more than the $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$) confirmed by the ERDT results. Moreover, the $\cdot\text{O}_2^-$ radical played an important role in the photocatalytic degradation of phenol. Thus, the modification of Mt/TiO₂ composites by Fe(III) can be an alternative material for the photocatalytic treatment of water pollutants.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11121381/s1>, Figure S1: Photocatalytic degradation and kinetics of phenol by Fe/Mt/TiO₂ synthesized at 70, 80 and 90 °C; Figure S2: XRD patterns of TiO₂, Fe/Mt/TiO₂ and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$ synthesized at 70, 80 and 90 °C; Figure S3: XPS (a) survey, narrow scans of (b) Ti 2p, (c) Fe 2p, (d) C 1s (e) O 1s, and (f) Si 2p orbitals for Fe/Mt/TiO₂; Figure S4: XPS (a) survey, narrow scans of (b) Ti 2p, (c) Fe 2p, (d) C 1s (e) O 1s, and (f) Si 2p orbitals for $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$; Table S1: Parameters of XRD peak fitting of Fe/Mt/TiO₂ and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$; Table S2: Parameters of pseudo-first-order kinetics for the photocatalytic degradation of phenol on TiO₂, Fe/Mt/TiO₂ and $x\text{Fe-Mt}/(1-x)\text{Fe-TiO}_2$.

Author Contributions: L.Z.: conceptualization, investigation, formal analysis, writing—original draft, review, and editing; C.C.: formal analysis; V.B.: formal analysis; B.O.: investigation; K.S.: conception, interpretation, and editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Japan Society for the Promotion of Science (JSPS), KAKENHI (A) [No. JSPS JP19F19393]; Cooperative Research Programs at Hokkaido University Institute for Catalysis [Nos. 18A1001, 19B1002, 20A1001, and 21A1001]; and Kyushu University (Progress 100) to K.S. This work was supported by the nanotech platform at Kyushu University with proposal no. S-20-KU-0001.

Acknowledgments: The authors would like to thank the Nanotech Center, Kyushu University for XPS measurements.

Conflicts of Interest: The authors declare no conflict of interest.

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