

Effects of Fe content on photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$

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Abstract: $\text{CaTiO}_3\text{-Fe}_x$ was characterized by X-ray diffractometry, scanning electron microscopy equipped with an energy dispersive spectrometry system, Fourier transform infrared spectra, and UV-visible spectra. Effects of Fe content on photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$ were investigated through measuring photocatalytic degradation rate of methylene blue. The results show that chemical compositions of $\text{CaTiO}_3\text{-Fe}_x$ remained unchanged with increasing Fe content from 0 to 4.745%. However, the light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$ exhibited a significant increase with increasing Fe content. Photocatalytic degradation of methylene blue over $\text{CaTiO}_3\text{-Fe}_x$ followed the first-order reaction kinetics. Based on changes of the concentration of methylene blue and its degradation kinetics, $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ has shown to have optimal photocatalytic activity. The degradation rate of methylene blue over $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ was almost 100% under UV-visible light irradiation for 3.0 h. The k_{obs} of methylene blue over $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ was 1.33 h^{-1} and was 7 times that over $\text{CaTiO}_3\text{-Fe}_0$.

Key words: $\text{CaTiO}_3\text{-Fe}_x$; methylene blue; photocatalytic activity; kinetics

1 Introduction

TiO_2 -based materials have attracted considerable interest in photocatalytic degradation of organic pollutants in air or water since photolysis of water at TiO_2 electrode was first reported [1]. TiO_2 exhibited series of excellent properties such as chemical stability, high photocatalytic reactivity, and nontoxicity [2–5]. Due to its wide band gap energy (3.2 V), however, TiO_2 only showed photocatalytic activity under the UV light while it was inactive under the visible light. To enhance light absorption ability of TiO_2 in the visible light region, therefore, great efforts have been performed, such as doping of metal or nonmetal elements, surface modification, and coupling with other semiconductors.

In recent years, various photocatalysts including $\text{A}_2\text{B}_2\text{O}_7$ and W-based materials have been studied to achieve effective utilization of the solar energy [6–9]. Particularly, perovskites exhibited excellent photocatalytic activity and have been widely reported. The compositions of A and B sites in perovskite structure with a general formula of ABO_3 can be varied to change the electronic structure, optical property, and electrical

property. Photocatalytic degradation or destruction of organic or gaseous pollutants over SrTiO_3 -based materials has been investigated in detail [10–12]. It was reported that the Fe-doped SrTiO_3 had a much higher photocatalytic activity than SrTiO_3 for photocatalytic degradation of RhB under visible light irradiation [10]. Enhancement on the photocatalytic activity of TiO_2 by supporting of SrTiO_3 for decolorization of methylene blue was confirmed by TSUMURA et al [11]. SULAEMAN et al [12] demonstrated that nitrogen-doped SrTiO_3 showed excellent photocatalytic activity for the NO_x destruction under both UV and visible light irradiation.

It should be pointed out that CaTiO_3 was also an important one of perovskite-type materials. However, few of papers reported photocatalytic activity of CaTiO_3 [13,14]. Additionally, the doping of the Fe element was usually used to modify structures and enhance photocatalytic activities of various photocatalysts. In this work, therefore, $\text{CaTiO}_3\text{-Fe}_x$ was prepared and characterized in detail through the combined use of XRD, SEM-EDS, FTIR spectra, and UV-Vis spectra. Effects of Fe content on photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$ were investigated through evaluating the

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degradation of methylene blue (MB) under UV-visible light irradiation. The degradation kinetics of MB over $\text{CaTiO}_3\text{-Fe}_x$ was also discussed using the first-order reaction mode.

2 Experimental

2.1 Preparation of $\text{CaTiO}_3\text{-Fe}_x$

CaTiO_3 was synthesized through the reaction of CaCO_3 and TiO_2 at 1400 °C. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ of 2.020 g was exactly weighed and dissolved in 100 mL ethanol. A certain volume of $\text{Fe}(\text{NO}_3)_3$ solution was sampled and diluted with ethanol. And then, $\text{Fe}(\text{NO}_3)_3$ solution was mixed with CaTiO_3 of 5.000 g and stirred to dry ethanol. Finally, the mixture was roasted to prepare $\text{CaTiO}_3\text{-Fe}_x$ (x was the mass fraction of the Fe accounting for CaTiO_3) at 500 °C. The x varied in the range of 0–4.745%.

2.2 Characterization methods

Chemical compositions of $\text{CaTiO}_3\text{-Fe}_x$ were analyzed using X-ray diffractometer (XRD, DX-2600) with Cu K_α radiation under 40 kV and 300 mA. The scanned range was $2\theta=20^\circ\text{--}65^\circ$ with a step of $2\theta=0.05^\circ$ and 1 s/step. A scanning electron microscope (SEM, S-3400N) equipped with an energy dispersive spectrometer (EDS) system was used to investigate the morphology and elemental compositions of $\text{CaTiO}_3\text{-Fe}_x$. The functional groups were studied using the Fourier transform infrared spectra (FT-IR, Thermo Nicolet-380) with KBr as a reference. The light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$ was measured through a UV-visible spectrophotometer (UV-Vis, UV-2550).

2.3 Photocatalytic degradation of MB over $\text{CaTiO}_3\text{-Fe}_x$

0.1 g of $\text{CaTiO}_3\text{-Fe}_x$ was dispersed into 100 mL of 5×10^{-6} MB aqueous solution in quartz vessel. The solution pH was adjusted to 11 with 1 mol/L NaOH solution since it has been confirmed that the solution pH of 11 was the optimal for photocatalytic degradation of MB over CaTiO_3 [13]. To reach an adsorption/desorption equilibrium of MB over $\text{CaTiO}_3\text{-Fe}_x$, the aqueous suspension was magnetically stirred for 30 min in the dark. A 500 W Hg lamp with 365 nm dominant wavelength was extended into the aqueous suspension and employed as the UV-visible light source. The temperature was kept at 25 °C by circulating cooling water during the reaction. At a certain interval, aqueous suspension of 5 mL was sampled and centrifuged for 10 min at a rate of 3000 r/min in the centrifuge. The changes of MB concentration as a function of irradiation time were determined by measuring the absorbance of the solution at 664 nm (the maximum absorption

wavelength for MB) using the UV-visible spectrophotometer (UV-Vis, UV-2550). The photo-degradation rate (η) of MB was described as $\eta=1-C_t/C_0$, where t is the reaction time, and C_0 and C_t are the initial concentration of MB and concentration of MB at time t , respectively.

3 Results and discussion

3.1 Characterizations of $\text{CaTiO}_3\text{-Fe}_x$

As shown in Fig. 1, $\text{CaTiO}_3\text{-Fe}_x$ exhibited diffraction peaks at 2θ of 23.156° , 33.060° , 40.966° , 47.457° , and 59.274° . According to the JCPDS database (No. 08-0091), these peaks were assigned to CaTiO_3 with a perovskite-type structure of cubic symmetry. It was noticed that diffraction peaks of $\text{CaTiO}_3\text{-Fe}_x$ almost remained unchanged with increasing Fe content from 0 to 4.745%. It should be pointed out that Fe^{3+} (0.79 Å) and Ti^{4+} (0.75 Å) have similar ionic radius, which may cause the exchange of Fe^{3+} and Ti^{4+} in CaTiO_3 and the formation of new perovskite-type species. Some of the Fe may also exist in Fe_2O_3 from the decomposition of $\text{Fe}(\text{NO}_3)_3$ during the calcination process. However, these Fe-containing species were not detected by XRD, which can be ascribed to the low content of these species in $\text{CaTiO}_3\text{-Fe}_x$.

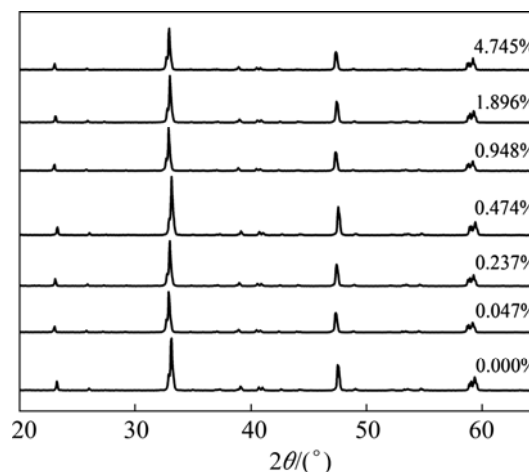


Fig. 1 XRD patterns of $\text{CaTiO}_3\text{-Fe}_x$

As shown in Figs. 2(a)–(g), the sizes of $\text{CaTiO}_3\text{-Fe}_x$ particles were in the range of 1–5 μm and almost remained unchanged with increasing Fe content in the range of 0–4.745%. $\text{CaTiO}_3\text{-Fe}_x$ particles exhibited similar morphology with the irregular polygon and smooth curved surface. Compared with $\text{CaTiO}_3\text{-Fe}_0$, $\text{CaTiO}_3\text{-Fe}_x$ (x was in the range of 0.047%–0.475%) showed a certain aggregate phenomenon, which can be intensified with increasing Fe content. In addition, Fe was not detected in the EDS result of $\text{CaTiO}_3\text{-Fe}_0$ (Fig. 2(h)) while it was found in the EDS result of

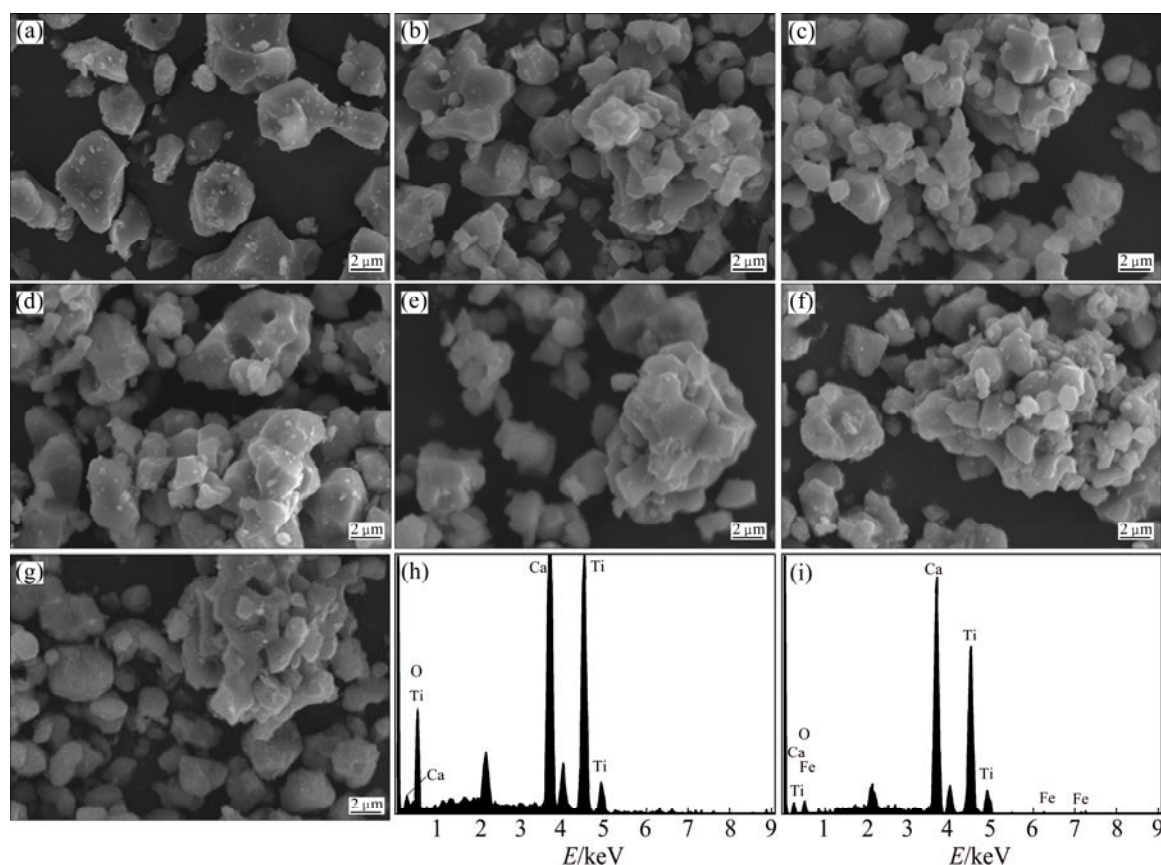


Fig. 2 SEM mages of $\text{CaTiO}_3\text{-Fe}_0$ (a), $\text{CaTiO}_3\text{-Fe}_{0.047\%}$ (b), $\text{CaTiO}_3\text{-Fe}_{0.237\%}$ (c), $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ (d), $\text{CaTiO}_3\text{-Fe}_{0.948\%}$ (e), $\text{CaTiO}_3\text{-Fe}_{1.896\%}$ (f), and $\text{CaTiO}_3\text{-Fe}_{4.745\%}$ (g) and EDS results of $\text{CaTiO}_3\text{-Fe}_0$ (h) and $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ (i)

$\text{CaTiO}_3\text{-Fe}_{0.474\%}$ (Fig. 2(i)). This demonstrates that Fe exists on the surface or in the lattice of $\text{CaTiO}_3\text{-Fe}_x$ particles.

Figure 3 summarizes FTIR spectra of $\text{CaTiO}_3\text{-Fe}_x$. Peaks at 3400 cm^{-1} and 1650 cm^{-1} were assigned to the functional group O—H in H_2O [15], and the peak at 1456 cm^{-1} was related to the functional group N—H [16]. The peak at 570 cm^{-1} was ascribed to Ti—O stretching and Ti—O—Ti bridging stretching modes [17]. The exchange of Fe and Ti in CaTiO_3 or Fe_2O_3 from the decomposition of $\text{Fe}(\text{NO}_3)_3$ should result in the formation of Ti—O—Fe and Fe—O bands. However, Ti—O—Fe and Fe—O bands were not detected in FTIR spectra. This may be related to the lower content of these species than the detection limit of FTIR spectra.

Figure 4 shows UV-Vis diffusive reflectance spectra of $\text{CaTiO}_3\text{-Fe}_x$. Compared with $\text{CaTiO}_3\text{-Fe}_0$, the light absorption ability of $\text{CaTiO}_3\text{-Fe}_{0.047\%}$ exhibited an increase in the range of 350–450 nm. With increasing Fe content from 0.047% to 4.475%, the light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$ significantly increased in the UV and visible light region. The exchange of Fe and Ti may form isolated energy levels in CaTiO_3 , reducing necessary energy of electron transition and enhancing the light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$. Additionally, XIE

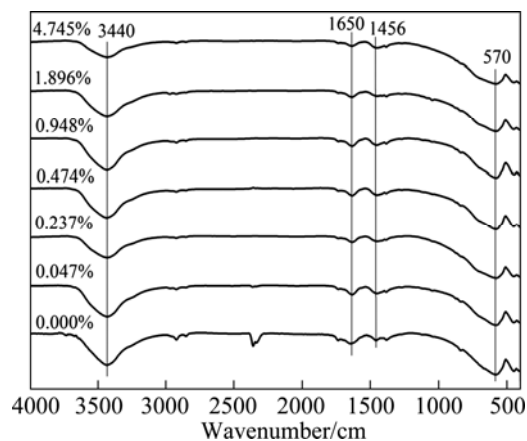


Fig. 3 FTIR spectra of $\text{CaTiO}_3\text{-Fe}_x$

et al [10] have found the presence of the visible light excitation of $\text{Ti}^{\text{IV}}\text{-O-Fe}^{\text{II}}$ to $\text{Ti}^{\text{III}}\text{-O-Fe}^{\text{III}}$ in Fe-doped SrTiO_3 . The electronic band structure of CaTiO_3 is similar to that of SrTiO_3 . Therefore, it should be the reasonable inference that the charge transfer excitation of $\text{Ti}^{\text{IV}}\text{-O-Fe}^{\text{II}}$ to $\text{Ti}^{\text{III}}\text{-O-Fe}^{\text{III}}$ in $\text{CaTiO}_3\text{-Fe}_x$ may also occur and contribute to the increase in the light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$. It was also noticed that the UV-Vis diffusive reflectance spectra of $\text{CaTiO}_3\text{-Fe}_{4.475\%}$ was obviously different from that of

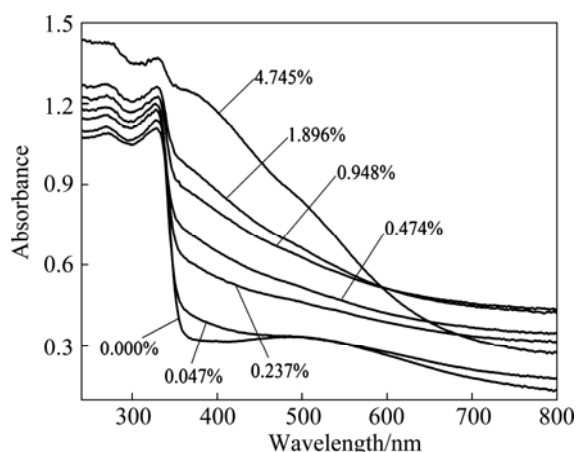


Fig. 4 UV-Vis diffusive reflectance spectra of $\text{CaTiO}_3\text{-Fe}_x$

other $\text{CaTiO}_3\text{-Fe}_x$ (x was in the range of 0–1.896%). This may be related to the formation of more Fe_2O_3 during the calcination process when Fe in $\text{Fe}(\text{NO}_3)_3$ accounted for 4.475% of CaTiO_3 .

3.2 Photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$

Figure 5 shows changes in the concentration of MB over $\text{CaTiO}_3\text{-Fe}_x$ under UV-visible light irradiation. After irradiation for 3.0 h, the degradation rate of MB over $\text{CaTiO}_3\text{-Fe}_0$ was 44.5% while that over $\text{CaTiO}_3\text{-Fe}_{0.047\%}$ was 64.1%, suggesting that the doping of Fe element can greatly enhance the photocatalytic activity of CaTiO_3 . When there was not photocatalyst in the aqueous solution, the degradation rate of MB was just 13% under irradiation for 3.0 h. This demonstrates that the degradation of MB can be mainly ascribed to the photocatalytic role of $\text{CaTiO}_3\text{-Fe}_x$. Particularly, the degradation rate of MB over $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ almost reached 100% under irradiation for 3.0 h. However, the degradation rate of MB over $\text{CaTiO}_3\text{-Fe}_x$ greatly decreased with increasing Fe content from 0.948% to 4.745%. For example, the degradation rate of MB over $\text{CaTiO}_3\text{-Fe}_{4.745\%}$ was just 14.3% at the irradiation time of

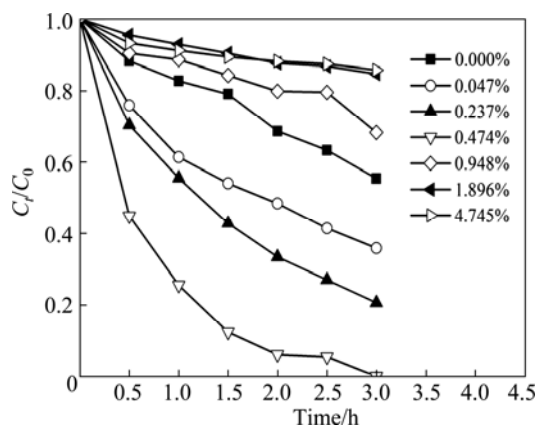


Fig. 5 Photocatalytic degradation of MB over $\text{CaTiO}_3\text{-Fe}_x$ under UV-visible light irradiation

3.0 h. With increasing Fe content, change of photocatalytic degradation of MB over $\text{CaTiO}_3\text{-Fe}_x$ was similar to that of MB over Fe-doped diopside [18].

The changes in the concentration of MB over $\text{CaTiO}_3\text{-Fe}_x$ were exponential as a function of irradiation time, suggesting that the reactions were reasonably described by the first-order kinetics as shown in Eq. (1).

$$\ln(C_t/C_0) = -k_{\text{obs}}t \quad (1)$$

where C_t is the concentration of MB at the time t , C_0 is the initial concentration of MB, and k_{obs} is the apparent rate constant of the first-order reaction. Figure 6 shows fitting results of changes in the concentration of MB over $\text{CaTiO}_3\text{-Fe}_x$ under irradiation. As shown in Fig. 6, the relationship between the natural logarithm of the concentration and irradiation time exhibited a linear correlation, demonstrating the first-order reaction nature of MB over $\text{CaTiO}_3\text{-Fe}_x$. The change trend of k_{obs} was similar to that of MB concentration as a function of Fe content. The k_{obs} of MB over $\text{CaTiO}_3\text{-Fe}_x$ significantly increased with increasing Fe content from 0 to 0.474%. The k_{obs} of MB over $\text{CaTiO}_3\text{-Fe}_0$ was 0.19 h^{-1} while that over $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ was 1.33 h^{-1} . The latter is 7 times the former. This further confirms that the doping of the Fe element with appropriate content can significantly enhance photocatalytic activity of CaTiO_3 . However, the k_{obs} of MB over $\text{CaTiO}_3\text{-Fe}_x$ drastically decreased when the Fe content was more than 0.948%. The k_{obs} of MB over $\text{CaTiO}_3\text{-Fe}_{4.745\%}$ was 0.06 h^{-1} and was lower by 68.4% than that over $\text{CaTiO}_3\text{-Fe}_0$, suggesting that the doping of excessive Fe can restrain photocatalytic activity of CaTiO_3 .

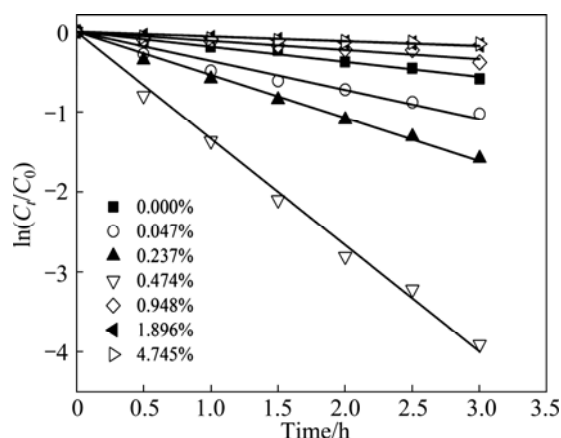


Fig. 6 Plot of $\ln(C_t/C_0)$ against irradiation time for $\text{CaTiO}_3\text{-Fe}_x$

The light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$ increased with increasing Fe content (Fig. 4), whereas there was an optimal Fe content for photocatalytic degradation of MB over $\text{CaTiO}_3\text{-Fe}_x$ (Figs. 5 and 6). For the Fe content less than 0.474%, the enhancement on the light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$ can contribute to

the increase of k_{obs} of MB with increasing Fe content. It should be pointed out that Fe_2O_3 from the decomposition of $\text{Fe}(\text{NO}_3)_3$ may hinder the interaction of MB with active sites on $\text{CaTiO}_3\text{-Fe}_x$. For the Fe content more than 0.948%, negative roles of Fe_2O_3 can be more significant than positive ones of the enhancement of the light absorption ability, resulting in the decrease of k_{obs} of MB over $\text{CaTiO}_3\text{-Fe}_x$ with increasing Fe content. Additionally, the agglomeration of $\text{CaTiO}_3\text{-Fe}_x$ particles was intensified with increasing Fe content (Fig. 2). When the Fe content was larger than 0.948%, serious agglomeration of $\text{CaTiO}_3\text{-Fe}_x$ particles can reduce the specific surface area of particles and block some active sites on $\text{CaTiO}_3\text{-Fe}_x$. This may also partly contribute to the decrease of k_{obs} of MB. YU et al [19] also observed similar results about effects of Fe content on photocatalytic activity of Fe-TiO_2 . They suggested that a small amount of Fe^{3+} can act as a temporary photo-generated electron or hole-trapping site and inhibit the recombination of photo-generated charge carriers [19]. Hydroxyl radicals ($\cdot\text{OH}$) was often assumed to be the major active species during the photocatalytic oxidation reaction [20]. Addition of moderate Fe^{3+} can promote the production of $\cdot\text{OH}$ and enhance photocatalytic degradation of organics. However, excess Fe^{3+} can become recombination centers of photo-generated electron and hole, which results in decrease of the activity of photocatalysts [19]. Certainly, the mechanism what roles the Fe element plays in the photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$ should be studied in detail in the further.

4 Conclusions

1) Based on XRD and FTIR spectra, it was confirmed that the Fe content in the range of 0–4.745% had little effect on chemical compositions of $\text{CaTiO}_3\text{-Fe}_x$. According to UV-Vis diffusive reflectance spectra, however, the light absorption ability of $\text{CaTiO}_3\text{-Fe}_x$ increased with increasing the Fe content.

2) Photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$ exhibited a significant increase with increasing the Fe content from 0 to 0.474%. Photocatalytic degradation rate of MB over $\text{CaTiO}_3\text{-Fe}_0$ was 44.5% while that over $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ was almost 100% under irradiation for 3.0 h. However, photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$ greatly decreased with increasing the Fe content from 0.948% to 4.745%. Photocatalytic degradation rate of MB over $\text{CaTiO}_3\text{-Fe}_{4.745\%}$ was only 14.3% under irradiation for 3.0 h. These results demonstrate that there is an optimal Fe content for photocatalytic activity of $\text{CaTiO}_3\text{-Fe}_x$.

3) Photocatalytic degradation of MB over $\text{CaTiO}_3\text{-Fe}_x$ exhibited the first-order reaction nature. It

was calculated that the k_{obs} of MB over $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ was 7 times that over $\text{CaTiO}_3\text{-Fe}_0$.

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铁含量对 $\text{CaTiO}_3\text{-Fe}_x$ 光催化活性的影响

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摘 要: 利用 XRD、SEM-EDS、FT-IR 光谱、UV-Vis 光谱等多种方法对 $\text{CaTiO}_3\text{-Fe}_x$ 进行表征, 通过测定亚甲基蓝的光催化降解率来考察铁含量对 $\text{CaTiO}_3\text{-Fe}_x$ 光催化活性的影响。结果表明, 当铁含量从 0 增加到 4.745% 时, $\text{CaTiO}_3\text{-Fe}_x$ 的化学组成几乎保持不变。但是, 随着铁含量的增加, $\text{CaTiO}_3\text{-Fe}_x$ 的光吸收能力显著增强。亚甲基蓝在 $\text{CaTiO}_3\text{-Fe}_x$ 上的光催化降解遵循一级反应动力学。基于亚甲基蓝浓度的变化及其反应动力学, $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ 显示出最佳的光催化活性。在紫外-可见光光照 3.0 h 时, 亚甲基蓝在 $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ 上的光催化降解达到 100%。亚甲基蓝在 $\text{CaTiO}_3\text{-Fe}_{0.474\%}$ 上光催化降解的表现速率常数(k_{obs})为 1.33 h^{-1} , 是其在 $\text{CaTiO}_3\text{-Fe}_0$ 上光催化降解的 k_{obs} 的 7 倍。

关键词: $\text{CaTiO}_3\text{-Fe}_x$; 亚甲基蓝; 光催化活性; 动力学

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