

# Photodegradation of Cinnamic Acid Solution in the Presence of Various Oxidizing Agents on TiO<sub>2</sub> and Fe-TiO<sub>2</sub> Catalysts

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**Abstract:** In this paper,  $TiO_2$  and Fe-doped  $TiO_2$  had been prepared by the sol-gel method. Physico-chemical characteristics of the catalysts were determined by the methods of BET Adsorption, XRD, FT-IR, and UV-Vis spectroscopies. Experimental results showed that the The modification of  $TiO_2$  catalyst with Fe led to reducing the crystallite size and PZC, and extending the spectrum of photon absorption to the visible region. The activity of obtained catalysts for photodegradation of cinnamic acid (CA) solution in the presence of various oxidizing agents ( $O_2$ ,  $O_3$  and  $H_2O_2$ ) was investigated and the optimum reaction conditions were identified. It follows that the addition of Fe additive is able to reduce the optimal catalyst concentration 3-5 times and increase the catalytic activity. It was found that  $O_3$  and  $H_2O_2$  agents showed the higher efficiency for cinnamic acid photodecomposition than usual  $O_2$ . In optimum conditions, after 90 minutes reaction, the conversion of cinnamic acid in the solution achieved 58.5, 77.7 and 83.1% on  $TiO_2$  and 85.7, 82.8 and 89.4% on Fe-TiO<sub>2</sub> in the presence of  $O_2$ ,  $O_3$  and  $H_2O_2$  respectively.

Key words: Photodegradation, cinnamic acid, oxidizing agents, TiO<sub>2</sub> and Fe-TiO<sub>2</sub>.

## 1. Introduction

Photocatalysis is an advanced process having many useful applications, particularly in environment cleanup [1]. Intrinsically, photocatalysis is refers to the reaction accelerated by light in the presence of catalyst, normally a semiconductor. In fact, TiO<sub>2</sub> is the best choice for commercial catalyst because of its high photocatalytic activity under UV irradiation, chemical and thermal stability, non-toxicity, reasonable band gap energy, easily available, and low cost. Up to now, compared to the other photocatalysts, TiO<sub>2</sub> has better performance and is preferable.

 $TiO_2$  in anatase phase, whose energy exceeds the band gap of 3.2 eV, could be activated under

ultraviolet light ( $\lambda < 387$  nm). However, it is broadly known that only 3-5 % of sunlight is UV-irradiation, capable to activate TiO<sub>2</sub> becoming a photocatalyst. Therefore, widening the light absorbing zone of TiO<sub>2</sub>-based photocatalyst into visible range is really necessary. In addition,  $e^{-}/h^{+}$  recombination is a practical problem related to reduce quantum yield and need to be considered carefully. There are several ways to modify TiO2 including metal-ion implanted TiO<sub>2</sub> (using transition metals: Cu, Co, Cr, Mo, V, W, Fe, Ag, Au and Pt), composite TiO<sub>2</sub> with carbon nanotubes, dye sensitizers or other photo-sensitive semiconductors (e.g. CdS, ZnO), non-metal and metal doping [2]. As it follows from our previous investigation [3], Fe-doped TiO<sub>2</sub> has been considered as an effective dopant for photoactivity enhancement. Photocatalysts of pure and Fe-modified TiO<sub>2</sub> with a

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particle size of about 20-30 nm were prepared by the sol-gel method. Doping TiO<sub>2</sub> by iron enabled red shift the photon absorbing zone of TiO<sub>2</sub> (with  $\lambda$  up to 464 nm) and reduced the value of the band gap energy down to 2.67 eV [3]. Fe-modified TiO<sub>2</sub> catalysts showed advantages over the pure TiO<sub>2</sub> sample when operating in the photooxidation of p-xylene in gas phase under visible light radiation. The utilization of UV and visible light in a combined mode of irradiation for the catalyst Fe-doped TiO<sub>2</sub> increased its activity and degradation efficiency in the p-xylene photooxidation by up to two to three times with considerable stability [3].

The photodegradation of numerous organic compounds were investigated on TiO<sub>2</sub>, including pesticides and phenolic contaminants in wastewaters such phosphamidon diphenamid [4-8], as indole-3-acetic acid and indole-3-butyric acid [9], dimethoate [10], propham, propachlor and tebuthiuron [11], 4-chlorophenol and 2,6-dichlorophenol [12]); emerging contaminants in municipal wastewater (i.e. acetaminophen, antipyrine, atrazine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole and triclosan) [13, 14], dyes (reactive red 4, methylene blue [15-17], reactive red 222 [18], crystal violet [19], remazol black [16], methyl orange and congo red [20]), and herbicides (picloram [21] and imazethapyr [22]), etc.

Cinnamic acid  $(C_9H_8O_2)$  – an unsaturated carboxylic acid is one of the phenolic compounds commonly present in oil mill vegetation and washing wastewaters, where its concentration reaches up to 106 mg/L [23]. Many works have reported the degradation of this acid by several advanced oxidation processes (AOPs) including  $H_2O_2$  [24], Fenton processes (i.e.  $Cu^{2+}/H_2O_2$  [24],  $Fe^{2+}/H_2O_2$  [24, 25] or  $Fe^{2+}/H_2O_2$  under UV light [25]). However, much less is known about the treatment of cinnamic acid solutions by photocatalytic systems TiO<sub>2</sub>-UV.

Therefore, the scope of this work is to investigate

the effect of various oxidizing agents (i.e.  $O_2$ ,  $O_3$  and  $H_2O_2$ ) on the removal efficiency of cinnamic acid (CA) in model effluents on  $TiO_2$  and Fe-TiO<sub>2</sub> photocatalysts.

# 2. Materials

## 2.1. Preparation of Catalysts

Pure TiO<sub>2</sub> catalyst was prepared by the sol-gel method as follows: 15 mL of tetraisopropyl orthotitanate Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (TTIP) was added to an ethanol-HNO<sub>3</sub> mixture with a pH of about 3-4 and stirred for 10 minutes to obtain a transparent solution. The solution was added drop wise to 10 mL of deionized water, stirred at room temperature for 2 hours to form a highly viscous solution. The solution was standing for 24 hours to obtain a transparent soft gel. The sample was dried in three stages at room temperature, 80 °C and 100 °C for 2 hours at every stage. Finally, the calcination and crystallization were carried out at 450 °C for 2 hours in an air flow and then the powder TiO<sub>2</sub> was obtained and is denoted by TiO<sub>2</sub>.

TiO<sub>2</sub> catalyst doped 0.1 mol% Fe<sub>2</sub>O<sub>3</sub> was prepared by the sol-gel method according to above procedure, with a difference 10 mL of deionized water added drop wise was replaced by 10 mL Fe(NO<sub>3</sub>)<sub>3</sub> solution in deionic water. The powder Fe-doped TiO<sub>2</sub> was obtained and denoted as Fe-TiO<sub>2</sub>.

## 2.2. Physico-Chemical Characteristics Analyses

Physico-chemical characteristics of catalysts were investigated by various methods, including BET surface areas and pore volumes (N<sub>2</sub> physisorption), X-ray powder diffraction analysis (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), and UV-Vis absorption spectroscopy. The point of zero charge (PZC) of obtained catalysts was determined by acid-base titration method.

## 2.3. Photocatalytic Activity

Experiments for photocatalytic degradation of cinnamic acid in the presence of various oxidizing agents (O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) were carried out using the batch photocatalytic system illustrated in Fig. 1. Photocatalytic reactor is the inner quartz double-wall jacket with inlet and outlet for the water circulation to maintain the temperature of the reaction mixture. Reactor is designed with the volume of reaction solution of 250 mL and radium ralutec 9W/78 UVA G23 lamp (36 lamps,  $\lambda \approx 350$ -400 nm, Capacity each lamp 0.160 mW). The photo-reactor was isolated by using a thick plastic black cover. In addition, the reaction mixture is mixed by magnetic stirrer.

In all experiments, reaction solution volume 250 ml, cinnamic acid concentration 50 mg/L and stirring 250 rpm were fixed. Influences of catalyst concentration and operation parameters (i.e. initial solution pH, temperature of reaction solution and dissolved oxygen (DO) or flow rate of  $O_3$  supply or  $H_2O_2$  concentration) on the photoactivity of catalysts were investigated. The catalysts were separated by filtration (syringe filter, pore size 0.22 µm, sarttorius NY) from the aqueous solutions prior to analyzing the

samples. The concentrations of cinnamic acid (CA) in the solution were determined by UV-visible spectrophotometer (UV-1800, Shimadzu, Japan) at  $\lambda_{max} = 272$  nm.

## 3. Results and Discussion

#### 3.1 Physico-Chemical Characteristics of Catalysts

The XRD spectra as well as the Raman spectra of catalysts showed that TiO<sub>2</sub> only existed in anatase phase. On XRD spectra of both catalysts (Fig. 2), characteristic peaks of TiO<sub>2</sub> anatase phase appeared at  $2\theta = 25.3^{\circ}$ ,  $37.8^{\circ}$ ;  $48.1^{\circ}$ ;  $55.1^{\circ}$  and  $62.7^{\circ}$  with the strongest intensity at  $2\theta = 25.3^{\circ}$ . The characteristic peaks of rutile phase  $(2\theta = 26.9^{\circ}, 35.7^{\circ}, 40.8^{\circ}, 53.7^{\circ})$ 55.8° and 63.5°) [26] almost did not appear. According to authors [27], Fe-TiO<sub>2</sub> catalyst only converted anatase to rutile phase when Fe concentration was more than 0.1 mol%. The intensity of the anatase peaks in Fe-doped  $TiO_2$  is higher than that of pure TiO<sub>2</sub> that indicated the crystallite of Fe-doped TiO<sub>2</sub> is better than TiO<sub>2</sub> catalyst. The authors [28] also obtained the same results and proposed the incorporated Fe into TiO<sub>2</sub> did not change the crystal structure of  $TiO_2$  due to probably  $Ti^{4+}$  ions in the crystal framework of TiO<sub>2</sub> was replaced by Fe<sup>3+</sup> ions.





I - Liquid cooling system; II - UV-LED lamps controller (PC adapter); III - Magnetic stirrer; IV - Cooling water tank; V - Circulation pump; VI - Air pump; VII - Flow meter; VIII - ; IX - Thermometer; X - Reactor; 1, 2 - Liquid coolant pipeline; 3, 4 - Water pipeline; 5- Air/ozone pipeline.



Fig. 2  $\,$  XRD spectra of  $TiO_2\left(a\right)$  and Fe-TiO\_2\left(b\right) catalysts.

On the Raman spectra of the catalysts (Fig. 3) appeared four characteristic peaks for anatase phase of TiO<sub>2</sub> at 153, 395, 520 and 643 cm<sup>-1</sup>. In which,  $E_g$  peaks at 153 cm<sup>-1</sup> and 643 cm<sup>-1</sup>,  $B_{1g}$  at 395 cm<sup>-1</sup> and  $A_{1g}$  at 520 cm<sup>-1</sup> were observed.  $E_g$  peaks are formed mainly by fluctuating the symmetric stretch of O-Ti-O in TiO<sub>2</sub>,  $B_{1g}$  peaks are formed by bending oscillation of the O-Ti-O and  $A_{1g}$  are formed by bending the asymmetric oscillation of O-Ti-O [29]. No characteristic peaks of Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> was observed that is consistent with the results of the XRD analysis. It indicated that when Fe ions were incorporated into TiO<sub>2</sub> crystal structure, species -TiO-Fe-O-Ti-O- type were formed [30].

It can be found from TEM images (Fig. 4) that both samples consist of pseudo spherical particles, but the particle size of TiO<sub>2</sub>-Fe catalyst was smaller and more uniform than TiO<sub>2</sub>. Nanoparticle size of TiO<sub>2</sub> and Fe-TiO<sub>2</sub> was about 25 nm and 9.2 nm, respectively. As such, modification TiO<sub>2</sub> by Fe has significantly reduced the size of catalyst particles, leading to an increase in surface area of catalyst from 43.6 m<sup>2</sup>/g to 90.5 m<sup>2</sup>/g.

The FT-IR spectra (Fig. 5) of both catalysts showed the characteristic peaks of basic OH-groups on TiO<sub>2</sub> surface at ~3,350 cm<sup>-1</sup> and adsorbed water molecules (1,630 cm<sup>-1</sup>). The peaks at 400-700 cm<sup>-1</sup> may be attributed to the vibration of Ti-O-Ti and Ti-O or Fe-O. In comparison with pure TiO<sub>2</sub>, Fe-TiO<sub>2</sub> sample showed a higher intensity of the peak corresponding to OH-groups on catalyst surface probably due to its higher surface area, leading to more water adsorbed on the catalyst surface to generate OH-groups.

UV-vis diffuse reflectance spectra of catalysts (Fig. 6)



Fig. 3 Raman spectra of  $TiO_2$  (a) and  $Fe-TiO_2$  (b) catalysts.



Fig. 4 TEM images of TiO<sub>2</sub> (a) and Fe-TiO<sub>2</sub> (b) catalysts.



Fig. 5 FT-IR spectra of  $TiO_2$  (full line)) and Fe-TiO<sub>2</sub> (dashed line) catalysts.



Fig. 6 UV–vis diffuse reflectance spectra of  $TiO_2$  (full line) and Fe-TiO<sub>2</sub> (dashed line) catalysts.



Fig. 7 Pre-adsorption ( $C_{cat} = 0.75 \text{ g/L}$ ) and photolysis (UV,  $\lambda = 365 \text{ nm}$ ) of cinnamic acid solution on TiO<sub>2</sub> catalyst ( $C_{CA} = 50 \text{ mg/L}$ , pH = 7, T = 25 °C, DO = 7,6 mg/L).

indicated that iron oxide doped into  $TiO_2$  enables to extend the region of the photon absorption zone of  $TiO_2$  towards the visible waves (from  $\lambda = 410$  nm to 437 nm) as well as to reduce its band gap energy from 3.03 eV down to 2.87 eV. It is also noticeable that pure  $TiO_2$  catalyst prepared by the sol-gel method has the lower band gap energy than pure  $TiO_2$  anatase and TiO<sub>2</sub>-P25 (3.2 eV) [31].

3.2 The Pre-adsorption and Photolysis of Cinnamic Acid Solution

According to Fig. 7, after the pre-adsorption in dark or photolysis (no catalyst, UV lighting) process, CA concentration in the solution stayed nearly unchanged. No adsorption of CA during 90 minutes adsorption process was observed. The effect of UV irradiation alone on the degradation of CA is also negligible.

# 3.3 Activity of Catalysts in Photocatalytic Degradation of Cinnamic Acid

3.3.1 Photocatalytic Degradation of CA Solution in Presence of Oxygen

According to our previous investigation, the optimal conditions of photocatalytic degradation CA solution in presence of oxygen on pure TiO<sub>2</sub> prepared by hydrothermal method (TiO<sub>2</sub>(H)) were determined as follows reaction temperature 25 °C, initial solution pH = 7, DO = 6.4 mg/L and catalyst concentration 0.75 g/L.

Fig. 8 showed that the activity of TiO<sub>2</sub> catalyst prepared by the sol-gel method (TiO<sub>2</sub>(S)) was higher than that of one prepared by the hydrothermal method (TiO<sub>2</sub>(H)). This could be explained that TiO<sub>2</sub>(S) sample existed in the smaller and more uniform particle size (20-25 nm compare to 30-40 nm) and characterized by the lower band gap energy in comparison with TiO<sub>2</sub>(H) (Eg = 3.14 eV). After 90



Fig. 8 The conversion of CA solutions on pure  $TiO_2$  catalyst prepared by hydrothermal  $(TiO_2(H))$  and sol-gel method  $(TiO_2(S))$  in presence of  $O_2$ .

minutes reaction, CA conversion on  $TiO_2(S)$  and  $TiO_2(H)$  catalysts reached 58.5% and 48.5%, respectively.

On Fe-TiO<sub>2</sub> catalyst, conversion of cinnamic acid decreased with increasing of pH solution from 3.8 to 7 was observed from Fig. 9a. At pH of 3.8 and 5, the 90 minutes conversion of CA ( $X_{90}$ ) reached 80.4% and 75.9%, respectively, meanwhile at pH = 7, it reduced to 17%.

The variation of CA conversion with catalyst concentration has extreme character; the maximum CA conversion after 90 minutes reaction of 80.4% was observed at 0.75 g/L (Fig. 9b).

Fig. 9c showed that CA conversion almost did not change when the dissolved oxygen increased from 5.4 to 6.4 mg/L, the 90 minutes conversion of CA reached approximately 85%. However, when the dissolved oxygen increased up to 7.0 mg/L, CA conversion

reduced. Dissolved oxygen plays an important role in  $TiO_2$  photocatalytic reaction to assure sufficient electron scavengers present to trap the excited conduction-band electron from the recombination [32]. However, too intensive oxygen flow led to appearance of foams, that on one hand interferes with the absorption of UV light by reaction solution, on the other hand a part of catalyst particles move to the surface of the solution with air bubbles, that reduced the amount of catalyst in solution, in the result efficient handling of CA reduced [33].

Fig. 9d showed that with increasing the reaction temperature CA conversion increased little. The value of  $X_{90}$  reached 80, 85 and 87% corresponding to the reaction temperature 25, 30 and 35 °C. Therefore, the ambient temperature of 30 °C was chosen for the CA photodegradation with oxygen agent on Fe-TiO<sub>2</sub> catalyst.



Fig. 9 The conversion of CA solutions on Fe-TiO<sub>2</sub> catalyst in presence of  $O_2$ .

3.3.2 Photocatalytic Degradation of CA Solution in Presence of Ozone

Figs. 10 and 11 showed that compared to oxygen oxidant ozone had not only significantly reduced the concentration of used catalysts but also increased CA conversion. On TiO<sub>2</sub> catalyst, CA conversion rise from 59% to 82% when the flow rate of O<sub>3</sub> increased from 0.1 to 0.5 L/min (seen in Fig. 10(a)), but if ozone flow was still increased to 0.7 L/min, a decrease of X<sub>90</sub> down to ~79% was observed. This may be due to ozone supporting the production of O<sub>2</sub> and OH\* radicals (Eqs. (1)-(4)) [34]. However, excess O<sub>3</sub> reacts

with OH\* radicals to reduce the amount of radicals (Eq. 5) [35], leading to drop CA conversion.

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$O_3 + e^- \to O_3^{*-}$$
 (2)

$$O_3^{*-} + H^+ \to HO_3^*$$
 (3)

$$\mathrm{HO}_{3}^{*} \to \mathrm{O}_{2} + \mathrm{OH}^{*} \tag{4}$$

$$OH^* + O_3 \rightarrow O_2 + HOO^*$$
 (5)

 $Fe-TiO_2$  catalyst exhibited the higher photoactivity than  $TiO_2$  and it reached the maximum CA conversion



Fig. 10 The conversion of CA solutions on TiO<sub>2</sub> catalyst in presence of ozone: (a) effect of ozone flow ( $C_{cat} = 0.75 \text{ g/L}$ , pH = 7, T = 25 °C), (b) effect of catalyst concentration ( $Q_{ozone} = 0.3 \text{ L/min}$ , pH = 7, T = 25 °C), (c) Effect of initial pH solution ( $C_{cat} = 0.75 \text{ g/L}$ ,  $Q_{ozone} = 0.3 \text{ L/min}$ , T = 25 °C) and (d) effect of reaction temperature ( $C_{cat} = 0.75 \text{ g/L}$ ,  $Q_{ozone} = 0.3 \text{ L/min}$ , pH = 7).



Fig. 11 The conversion of CA solutions on Fe-TiO<sub>2</sub> catalyst in presence of ozone: (a) effect of ozone flow ( $C_{cat} = 0.75 \text{ g/L}$ , pH = 7, T = 25 °C), (b) effect of catalyst concentration ( $Q_{ozone} = 0.3 \text{ L/min}$ , pH = 7, T = 25 °C), (c) effect of initial pH solution ( $C_{cat} = 0.75 \text{ g/L}$ ,  $Q_{ozone} = 0.3 \text{ L/min}$ , T = 25 °C) and (d) effect of reaction temperature ( $C_{cat} = 0.1 \text{ g/L}$ ,  $Q_{ozone} = 0.3 \text{ L/min}$ , pH = 5).

about 85% at as low O3 flow rate as 0.3 L/min (Fig. 11a). This may due to the facts that the energy level for  $Fe^{3+}/Fe^{4+}$  is above the valence band edge of  $TiO_2$  and the energy level for  $Fe^{3+}/Fe^{2+}$  is below the conduction band edge of TiO<sub>2</sub> [36], Fe<sup>3+</sup> ions acting as both electrons and holes traps can turn into Fe<sup>2+</sup> and Fe<sup>4+</sup> ions by trapping photogenerated electrons and holes, respectively. Fe<sup>2+</sup> ions can be oxided to Fe<sup>3+</sup> ions by transferring electrons to absorbed O<sub>2</sub> on the surface of TiO<sub>2</sub> or a neighboring surface Ti<sup>4+</sup> ions [37]. Meanwhile, the adsorbed  $O_2$  is reduced to  $O^{2-}$ , which can further degrade CA. Similarly, Fe<sup>4+</sup> ions also are reduced to Fe<sup>3+</sup> ions by releasing electrons, while surface hydroxyl group translates into OH\* radical. As a result, the introduction of appropriate Fe<sup>3+</sup> ions is responsible for the reduction of the photogenerated hole-electron recombination rate and favors the improvement of photocatalytic activity. However, Fe<sup>3+</sup> ion can act as the recombination centers for the photogenerated electrons and holes when Fe<sup>3+</sup> ion concentration becomes high, lead to the decrease of photocatalytic activity. In our case the optimal doping concentration is 0.1%. Above that concentration,  $Fe^{3+}$ ion steadily become recombination centers and the photocatalytic activity gradually decreases [38].

With increasing catalysts concentration, CA conversion increased strongly on pure  $TiO_2$  (Fig. 10b), meanwhile it just did slightly on Fe doped-TiO<sub>2</sub> (Fig. 11b). Thereby, it reducing significantly the required concentration of catalyst, thanks to the reduction of the particle size and the increase of specific surface area, moreover, the appearance Fe<sup>3+</sup> ions motived the formation of radicals O<sup>2-</sup>, HOO\* and OH\*, leading to intensify the activity of TiO<sub>2</sub>-Fe catalyst.

Like the case of using oxygen as oxidant in this case on pure  $TiO_2$  the CA conversion at pH = 7 was higher than that at pH = 5 and 9 (Fig. 10c), meanwhile, on Fe – doped TiO<sub>2</sub>, the conversion of CA is highest at acidic solution pH = 5 (Fig. 11c) were observed. Thus, doped Fe to  $TiO_2$  not only increases

the photocatalytic activity, but also alters the value of optimal initial pH of solution from neutral to acidic. This may due with the point of zero charge (PZC) of obtained  $TiO_2$  and Fe-TiO<sub>2</sub> was found of ~7.36 and 4.87 respectively. According to reports [39-41] the point of zero charge of  $TiO_2$  is the range of 4.5-7.0. At PZC point the interaction between the catalyst particles and CA solution is minimal due to the absence of any electrostatic force. When solution pH was below PZC, the catalyst surface of TiO<sub>2</sub> becomes positively charged (i.e.  $TiOH + H^+ \leftrightarrow TiOH_2^+$ ) and gradually exerted an electrostatic attraction force towards the negatively charged compounds. Such polar attractions between TiO<sub>2</sub> and charged anionic organic compounds can intensify the adsorption onto the photon activated TiO<sub>2</sub> surface for subsequent photocatalytic reactions [42]. At solution pH > PZC, the catalyst surface will be negatively charged (i.e.  $TiOH + OH^- \leftrightarrow TiO^- + H_2O$ ) and repulse the anionic compounds in water. Different pH will affect the surface charge density of TiO<sub>2</sub> catalyst [43].

Fe-TiO<sub>2</sub> catalyst favorable working in an acid environment can also cause it having higher activity than pure TiO<sub>2</sub>. Because in acidic solution the quantity of H<sup>+</sup> ions is much higher than that one with pH = 7, H<sup>+</sup> ions should be able to combine with O<sup>2-</sup> radicals to generate HOO\* radicals (Eqs. (6) and (7)) [44].

$$\operatorname{TiO}_{2}(e^{-}) + \operatorname{O}_{2} \to \operatorname{O}^{2^{-}} + \operatorname{TiO}_{2}$$

$$\operatorname{O}^{2^{-}} + \operatorname{H}^{+} \to \operatorname{HOO}^{*}$$

$$(6)$$

$$(7)$$

Moreover, the  $pK_a$  of CA is 4.4 [45], lower pH is consistent for the its photodegradation.

3.3.3 Photocatalytic Degradation of CA Solution in Presence of  $H_2O_2$ .

The influences of condition the CA conversion after 90 minutes reaction on both catalysts in the presence of  $H_2O_2$  were shown in Figs. 12 and 13.

The optimal conditions for CA photodegradation on both catalysts with various oxidizing agents are summarized in Table 1.

Figs. 12, 13 and Table 1 showed that on pure  $TiO_2$  catalyst in comparison with other oxidants ( $O_2$ ,  $O_3$ ),  $H_2O_2$ 



Photodegradation of Cinnamic Acid Solution in the Presence of

Fig. 12 The conversion of CA solutions on TiO<sub>2</sub> catalyst in presence of  $H_2O_2$ : (a) effect of  $H_2O_2$  concentration ( $C_{cat} = 0.75 \text{ g/L}$ , pH = 7, T = 25 °C), (b) effect of catalyst concentration ( $H_2O_2 = 1\%$ , pH = 5, T = 25 °C), (c) effect of initial pH solution ( $C_{cat} = 0.75 \text{ g/L}$ ,  $H_2O_2 = 1\%$ , T = 25 °C) and (d) effect of temperature reaction ( $C_{cat} = 0.75 \text{ g/L}$ ,  $H_2O_2 = 1\%$ , pH = 5).



Fig. 13 The conversion of CA solutions on Fe-TiO<sub>2</sub> catalyst in presence of  $H_2O_2$ : (a) effect of  $H_2O_2$  concentration ( $C_{cat} = 0.75$  g/L, pH = 7, T = 25 °C), (b) effect of catalyst concentration ( $H_2O_2 = 0.5\%$ , pH = 7, T = 25 °C), (c) effect of initial pH solution ( $C_{cat} = 0.1$  g/L,  $H_2O_2 = 0.5\%$ , T = 25 °C) and (d) effect of temperature reaction ( $C_{cat} = 0.1$  g/L,  $H_2O_2 = 0.5\%$ , pH = 5).

Table 1	The optimal conditions for	CA photodegradation	on TiO <sub>2</sub> - based	l catalysts using va	arious oxidizing agents.
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Catalyst	Oxidizing agent	Temperature (°C)	Catalyst concentration (g/L)	Value of Oxidizing agent	PH solution	Conversion after 90 minutes (%)
	O <sub>2</sub>	25	0.75	6.4 mg/L	7	58.5
TiO <sub>2</sub>	O <sub>3</sub>	25	0.75	0.3 L/min	7	77.7
	$H_2O_2$	25	0.50	1 %	5	83.1
	O <sub>2</sub>	30	0.75	5.4 mg/L	3.8	84.8
Fe-TiO <sub>2</sub>	O <sub>3</sub>	25	0.1	0.3 L/min	5	89.5
	$H_2O_2$	30	0.1	0.5 %	5	82.9

gave higher CA conversion and required lower catalyst concentration. This can be explained by that  $H_2O_2$  creating double OH\* radicals (Eqs. (8) and (9)) [46].

$$e^- + H_2O_2 \rightarrow OH^* + OH^-$$
 (8)

$$h^{+} + HO_{2} \rightarrow OH^{*} + H^{+}$$
(9)

Figs. 12 and 13 showed that at the optimal reaction conditions with the same oxidizing agent H<sub>2</sub>O<sub>2</sub>, to achieve the same CA conversion (~83%) the concentration of catalyst and H<sub>2</sub>O<sub>2</sub> in the case of using Fe-TiO<sub>2</sub> were much lower than those in case of using pure TiO<sub>2</sub> catalyst (seen in Table 1). The simultaneous presence of Fe<sup>3+</sup> ions in the catalyst and H<sub>2</sub>O<sub>2</sub> in reaction solution creating favorable conditions to increase the production of OH\* radicals by Fenton reaction (Eq. (10)) [46], but when concentration of Fe<sup>2+</sup> ions was too much the amount of radical OH\* reduced in the result of reaction (11) [47].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^-$$
 (10)

$$Fe^{2+} + OH^* \rightarrow Fe^{3+} + OH^-$$
(11)

Overall, the doping  $TiO_2$  by Fe leads to reduce the needed concentration of catalyst and oxidants, increasing CA conversion and allowing reactions proceed in acidic environment, the natural environment of the solution CA. In the photodegradation of CA, the absorption of CA on surface catalysts is medium.

## 4. Conclusions

Doping Fe to  $TiO_2$  causes the particle size reduction, red shift the photon absorbing zone of  $TiO_2$ and reduce its band gap energy from 3.03 eV to 2.87 eV that increased the photoactivity of Fe-TiO<sub>2</sub> catalyst. Using Fe-doped TiO<sub>2</sub> catalyst is able to reduce the optimal catalyst concentration 3-5 times, reduce oxidant concentration, increase catalytic activity and allows reaction process in acidic environment.

 $O_3$  and  $H_2O_2$  agents showed higher efficiency for cinnamic acid photodecomposition than usual  $O_2$ under UV-A light. In optimum conditions, after 90 minutes reaction, the conversion of cinnamic acid achieved 59-83% on  $TiO_2$  and on Fe-TiO<sub>2</sub> the CA conversion in reaction with all three oxidizing agents (O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) reached nearly 90%.

The results contributed to emphasize that pure  $TiO_2$ and Fe doped  $TiO_2$  catalysts prepared by sol-gel method have the great potential in photodecomposition of ring compounds and recalcitrant surfactants.

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