

Article

Studies on SnCl₂-doped TiO₂ Photocatalyst for Pyrocatechol Photodegradation

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Abstract. SnCl₂-doped TiO₂ photocatalyst for pyrocatechol photodegradation aimed to examine the effect of Sn/Ti ratio and H₂O₂+UVC irradiation. The preparation was carried out by the impregnation and the characterization consisted of WAXD, SEM, and laser particle size. Using 1 mM pyrocatechol in the CSTR with various TiO₂ photocatalysts, the remaining pyrocatechol was determined by UV-vis spectrophotometry to calculate % photodegradation. From WAXD results, it was found that SnO₂ incorporation to the TiO₂ bulk phase but the morphologies did not change. And the particle size changed due to the attraction force of the surface charging. Without H₂O₂ addition, it showed 15.7% photodegradation by TiSn10UVC compared to 11.37% of TiDark. Thus, UVC was the important factor for photodegradation. With H₂O₂+UVC irradiation, the maximum photodegradation reached 34.6% by TiSn10HOUVC, but those of HOUVC and TiHOUVC showed 25.0% and 26.5%, respectively. The Sn-doping affected the formation of more hydroxyl free radical from H₂O₂+UVC irradiation and charge separation. But higher Sn/Ti ration, it gave segregate SnO₂ which increased recombination center with the adverse effect on the lower photodegradation. The conclusion revealed that SnCl₂-doping with the ratio of Sn/Ti =10 onto TiO₂ photocatalyst showed the highest photoactivity with H₂O₂+UVC irradiation. Moreover, the chemical kinetics is also discussed.

Keywords: SnCl₂-doping, titanium dioxide, pyrocatechol photodegradation.

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1. Introduction

Pyrocatechol with IUPAC name of 1,2-dihydroxybenzene, it is the important precursor for production of pesticide and pharmaceuticals and fragrance, especially for vanillin. The production of vanillin by Rhodia Co. Ltd., it consumed pyrocatechol about 1,300 tons annually [1]. It is the hydrolysis product from 2-chlorophenol with alkali metal hydroxide catalyst [2]. Its toxicity is irritating to eyes, increasing blood pressure and kidney injury. And the pyrocatechol content of surface water is limited to 1 ppb by Environmental Protection Agency regulation [3]. The improper disposal of pyrocatechol from wastewater effluent, it will pollute the water resource and harm seriously to ecological system and human being. The problem demands the photocatalyst to solve. Among pyrocatechol remediation, there are Fenton, photo-Fenton and photocatalytic process [4]. Photocatalytic process showed higher activity for the Water pollution and Air purification. TiO_2 photocatalyst is the well known among researchers [5]-[8] since 1995. And its patents are already registered, for example US patent [9, 10]. Both publications and patents are not enough for all chemical pollutants since the specific molecular structure and the precise condition for photocatalysis has to find out from research firstly. Various TiO_2 photocatalysts were prepared for the specific polluting molecule under the certain condition.

Nanosize TiO_2 involved high cost of production and sophisticated method to produce in the large scale. Catalyst preparation will control the catalytic properties and its reactivity including the selection of transition metal doping [11]-[13]. There were many preparations ; precipitation , impregnation and coating of TiO_2 photocatalyst. From the precipitation method[14-16], the obtained catalysts had impurities and the composition was difficult to control. The coating was suitable for a small surface area and smooth substrate. Impregnation was suitable to produce from the small in lab to large quantity as in the pilot plant[16-17]. Additionally, it could apply to various shape of support. For example, 0.25 % Fe^{3+} -doped TiO_2 photocatalyst photodegraded 4-nitrophenol with 80 % conversion after 2hr [14]. Due to Fe^{3+} ion insertion to TiO_2 lattice and it also lowered the agglomeration of nanoparticle so it had higher efficiency [15, 16]. While Co-doped TiO_2 photocatalyst, it showed 100% of 4-chlorophenol removal at pH 10. Ceria lowered E_g with longer wavelength absorption and its photoactivity was higher than P-25 [17]. For V-doped TiO_2 photocatalyst prepared by sol-gel method, it could photodegrade 53% Congo red with sunlight and the reaction followed 1st order [18]. Additionally, V^{5+} could trap charge on the surface and led to hydroxyl free radical formation. $\text{SnO}_2/\text{TiO}_2$ photocatalyst had the oxidizing properties and gave 95% conversion for methyl orange [19]. But Sn-doped TiO_2 photocatalyst for pyrocatechol had the unclear point for the Sn/Ti ratio relating to its photocatalytic reactivity.

This research aims to examine the SnCl_2 doping on TiO_2 photocatalyst prepared by impregnation for pyrocatechol photodegradation. By varying the ratio of Sn/Ti and addition of H_2O_2 +UVC irradiation, they would give the optimum condition to obtain the highest photodegradation. Moreover, the catalyst characterization was carried out by WAXD, SEM and laser particle size. The information would support the relationship between the catalyst properties toward the photodegradation activity for pyrocatechol.

2. Experimental

2.1. Preparation of SnCl_2 -doped TiO_2 Catalyst

TiO_2 was supplied by Sigma Aldrich in AR grade and used without purification. The $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and H_2O_2 , they were supplied by Carlo Erba in AR grade. Pyrocatechol was supplied by Fluka in AR grade and it became the model pollutant in water. The dispersion of TiO_2 photocatalyst with 3.0 mL of distilled H_2O , it was carried out by vigorously stirring. And it was dried at 120°C 2 hr, and then the calcination took place at 500°C 6 hr under the ambient atmosphere. It was used as the control photocatalyst to compare the effect of SnCl_2 doping. The impregnation of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution onto the TiO_2 powder, it was conducted with the ratio of Sn: Ti of 5:100, 10:100 to 20:100, respectively. The impregnation method was already described [11-12]. After impregnation, the drying and calcination methods followed the previous method of TiO_2 without SnCl_2 doping. The obtained catalysts were white powder. They were symbolized as TiSn5, TiSn10, TiSn20. All of photocatalysts were tested photodegradation of pyrocatechol with UVC and H_2O_2 +UVC irradiation.

2.2. Characterization of SnCl₂-doped TiO₂ Photocatalyst

There were 2 types of photocatalysts, undoped TiO₂ and SnCl₂-doped photocatalysts. To identify the bulk phases, WAXD(Wide Angle X-ray Diffraction) spectroscopy was carried out with Mo K α =0.07106 nm and 17415.73 eV equipped by Lindermann glass capillaries at CEMES-CNRS, France. The measurements were conducted by graphite monochromators and two-axis diffractometers. Each sample took 20 h and the data were corrected for polarization and absorption effect. After normalization, Fourier-transformed methods, the data was obtained as radial distribution function. The diffractograms were plotted as 2 θ and their intensities. The JCPDS database was used to identify WAXD peaks. While, the experiment of SEM with 20,000 magnification was performed by JEOL modeled of JSM-5910LV to examine the surface morphologies at Electron Microscope Center-CMU, Thailand. All SnCl₂-doped TiO₂ photocatalysts were loaded on the carbon tape with gold sputtering. Then, the particle size of photocatalysts in the aqueous suspension within 5% wt, it was characterized by laser particle sizer supplied by Master Sizer-S supplied by Malvern Instrument Co. Ltd. The particle size analysis imitated the particle behavior similar as it suspended in photocatalysis system. Each experiment was carried out by the fresh photocatalyst to avoid the contamination on the surfaces. The research did not involve the used photocatalysts anymore.

2.3. Testing of Pyrocatechol Photodegradation by UVC Irradiation

1 mM 1 L of pyrocatechol solution as the model pollutant used in these experiments was transferred into the photoreactor as shown in Fig. 1 with the 15Wx 3 bulbs UVC irradiation. The luxmeter indicated 45 W of the light inside the photoreactor at the beaker position. Each experiment applied 1 g of photocatalyst and took 15 min vigorously stirring in a continuous stirred tank reactor. The control experiment was the dark experiment to clarify the effect of UVC irradiation. While, pyrocatechol photodegradation took 120 min and the sampling solution of 5 ml was pipetted for every 5 min. during the test. Then, the photocatalyst in the sampling solution was separated by the centrifuge to avoid the light scattering of residue photocatalyst particle. They were transferred to UV spectrophotometer to determine the UV absorbance of pyrocatechol and to compare with the initial pyrocatechol concentration. The % photodegradation were calculated by Eq. (1), and the analysis of the chemical kinetics was also included.

$$\% \text{ photodegradation} = \frac{C_0 - C_t}{C_0} * 100 = \left[1 - \left(\frac{C_t}{C_0} \right) \right] * 100 \quad (1)$$

where C₀ and C_t represented the initial concentration and instantaneous concentration of pyrocatechol, respectively. In order to study the effect of H₂O₂+UVC irradiation on pyrocatechol photodegradation, the H₂O₂ addition was constantly added at 3.7x10⁻³ mole. Their all symbolized as TiSn5HOUVC, TiSn10HOUVC and TiSn20HOUVC, respectively. These experiments could reveal the effect of H₂O₂+UVC irradiation on pyrocatechol photodegradation.

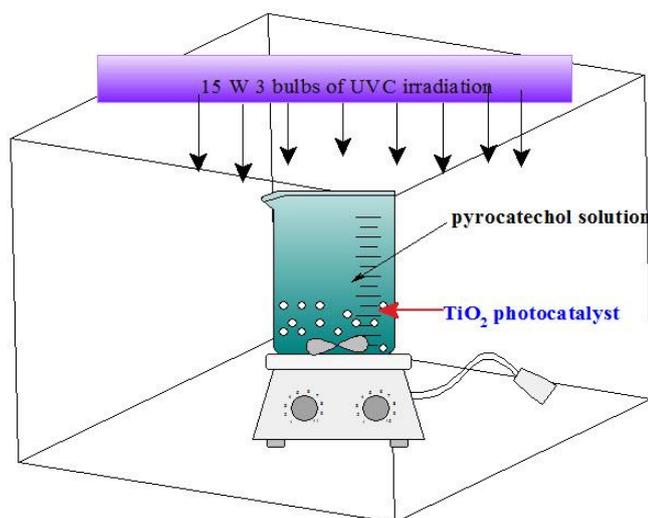


Fig. 1. Schematic diagram of the photoreactor for pyrocatechol photodegradation.

3. Results and Discussion

The results of WAXD, SEM and laser particle were shown in this section 3.1. Then, % photodegradation of pyrocatechol under UVC and $H_2O_2 + UVC$ irradiation, they were described in Section 3.2 including the chemical kinetics analysis, too.

3.1. Phase identification and morphologies of SnCl₂-doped TiO₂ photocatalysts

Figure 2 showed WAXD of various TiO₂ photocatalyst in this research, it was found that most peaks belonged to anatase phase assigned as A followed JCPDS no.21-1276. But the rutile phase was not found on the diffractograms anymore. These peaks were assigned as C belonged to SnO₂ peaks or cassiterite phase as JCPDS no. 41-1445. There was no peak of SnO anymore. It indicated that SnCl₂ or Sn²⁺ was reduced to Sn⁴⁺ as cassiterite and, then the chlorine ions were eliminated during calcination. The WAXD was in good agreement with the XRD results from Sasikala et al. report [20]. It informed that the impregnation method produced SnCl₂-doped TiO₂ photocatalyst successfully. With the ratio of Sn/Ti from 5% to 20%, these diffractograms also indicated that the higher intensities of cassiterite peaks increased as Sn/Ti ratio increased in the direct proportion way. It meant that more SnO₂ phase intimately mixed with bulk TiO₂ phases and incorporation in bulk phase due to their both tetragonal lattices. The Sn⁴⁺ ionic radius was 69 pm and Ti⁴⁺ of 61 pm. They both were in the same size so they could substitute at the crystal defect or vacant site on each other easily. To understand more information on morphology and particle size, it had been examined by SEM and Laser particle sizer for TiO₂ anatase phase with SnO₂ phase as shown in Figs. 2-3.

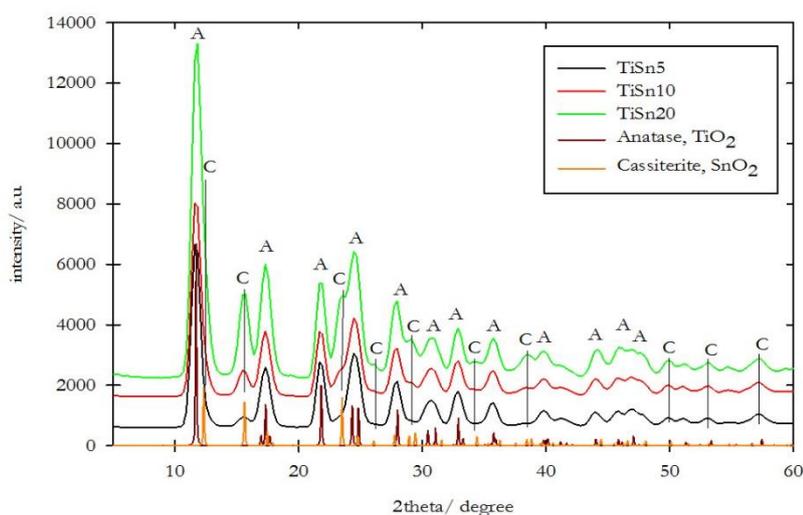


Fig. 2. Diffractograms of WAXD from SnCl₂-doped TiO₂ photocatalysts.

SEM images were illustrated in Fig 3(a)-Fig. 3(d) with x20,000 magnification from SnCl₂-doped TiO₂ photocatalyst, the morphology consisted of small facets exposed on the photocatalyst surface. The small crystallite of SnO₂ adhering on the TiO₂ surface resulted from the impregnation method. It dispersed evenly so it could improve the pyrocatechol photodegradation. Both TiO₂ and SnCl₂-doped TiO₂ photocatalyst, they had similar morphology. It meant that SnO₂ after calcination could substitute the TiO₂ defect on the surface. These morphologies corresponded to the previous research of K. Lee et al. [21] and C.K. Rhee et al. [22], respectively.

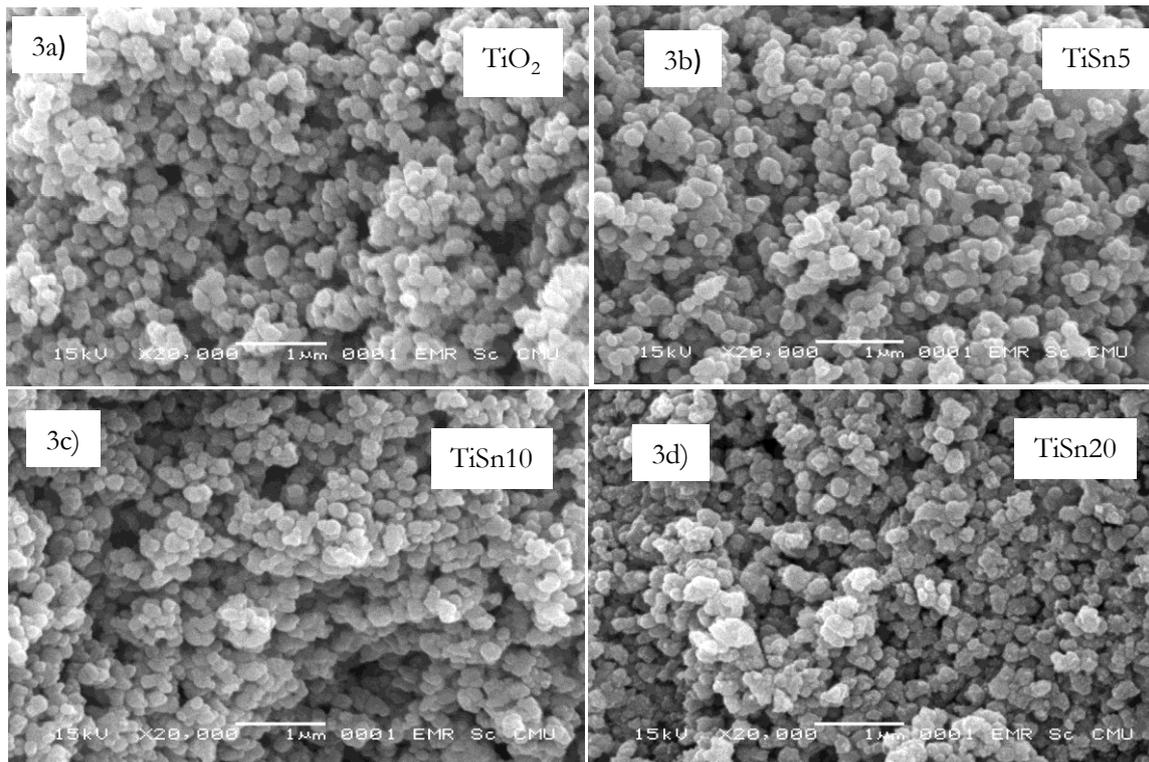


Fig. 3. Results from SEM of SnCl₂-doped TiO₂ photocatalysts. The blue arrows pointed at the SnO₂ crystals location on TiO₂ photocatalyst surface.

In Fig. 4(a)-4(d), there were 2 peaks representing the smaller and the larger agglomerates in all profiles of the particle size in Table 1. The undoped TiO₂ photocatalyst, it had the particle size of D [3, 4] of 2.48 micron as the smallest. After the Sn/Ti changed 5% to 20 %, their particle size changed to 21.64, 18.09, 134.85 micron, respectively. SnCl₂-doping increased the agglomeration size from 7.3 to 54.4 times. Similar to the transition metal doping on the oxide, it increased the particle size and agglomeration as the previous report [23, 24]. In case of Sn/Ti = 20%, it gave the most attraction force and large particles preferred to settle in the photodegradation testing. The presence of SnCl₂-doping, it caused more attraction force for the larger agglomeration in suspension. Additionally, SnCl₂-doping on TiO₂ photocatalyst gave the electrical double layer at the surface of the particle with surface charging and induced more agglomeration following DLVO(Derjaguin and Landau, Verwey and Overbeek.) interaction [25]. In this research, it did not include zeta potential measurements. The SnCl₂-doping also increased the particles size similar to the transition metal doping on oxide catalyst, it increased the particle size and agglomeration as the previous report [26]. Larger particle screened the UVC irradiation to the particle behind them as the shadow effect. And then, it would lower the photodegradation activity.

Table 1. Determination of particle size for TiO₂ and SnCl₂-doped TiO₂ photocatalysts.

Catalyst	Sn:Ti ratio	Particle size (μm)		
		Smaller size (μm)	Larger size (μm)	D[4,3] (μm)
TiO ₂	0	0.26	8.15	2.48
TiSn5	5	0.55	39.52	21.64
TiSn10	10	0.76	44.57	18.09
TiSn20	20	0.26	246.95	134.85

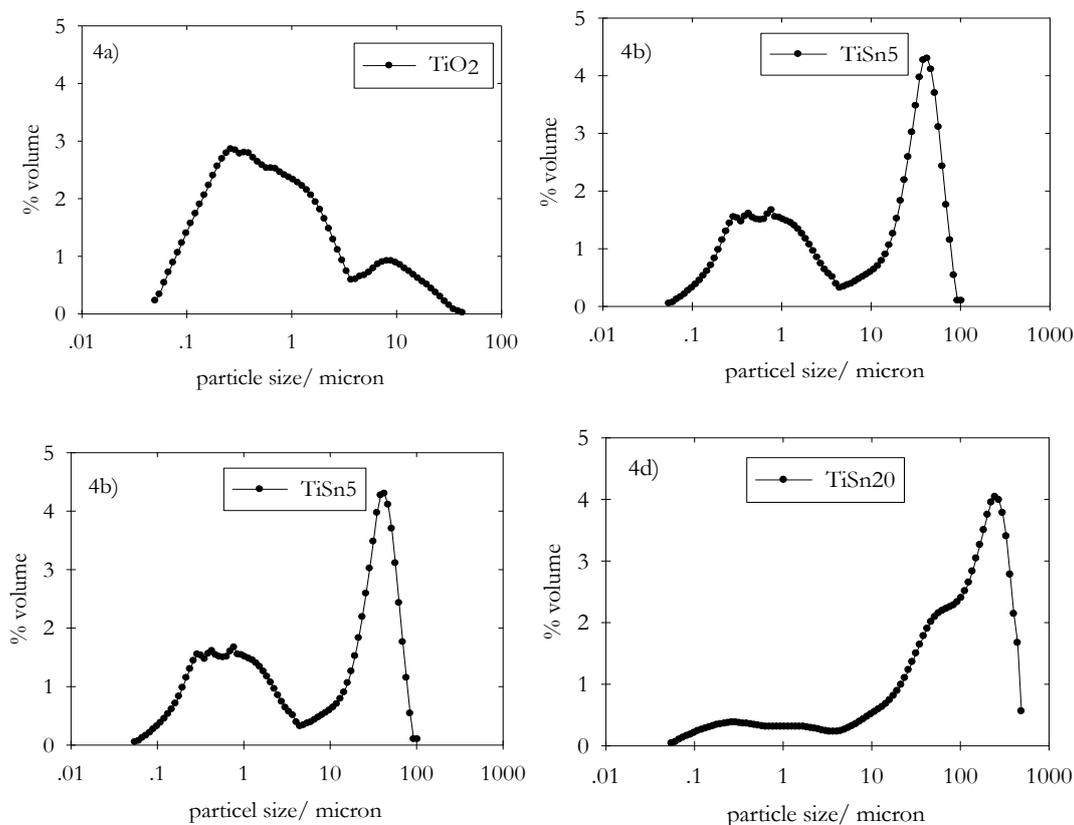


Fig. 4. Laser particle sizer of SnCl_2 -doped TiO_2 photocatalysts in aqueous suspension.

SnCl_2 -doping played role on the bulk phase changes from WAXD results. And the agglomeration particle size from laser particle sizer result in the suspension showed the larger particles more significantly than their morphologies from SEM images. Because of surface charging and it caused the attractive force from SnO_2 particle. Those results involved SnO_2 phase or cassiterite on TiO_2 photocatalyst. The effect of Sn-doping for photodegradation activity was showed in Fig. 5 for pyrocatechol photodegradation. It could occur on SnCl_2 -doped TiO_2 photocatalyst surfaces and showed the effect of Sn/Ti ratio with UVC irradiation. The combination of H_2O_2 +UVC irradiation will be shown in the next section.

3.2. Pyrocatechol photodegradation by UVC irradiation

From the characterization showed SnO_2 peaks on WAXD results, it meant that this method generated SnO_2 incorporated on TiO_2 bulk lattice. The photodegradation of these catalysts would show the reactivity in Fig. 5–7 to clarify the effect of Sn/Ti ratio and the addition of H_2O_2 on pyrocatechol photodegradation.

3.2.1. Effect of SnCl_2 -doping on TiO_2 photocatalyst

Using UVC irradiation for pyrocatechol photodegradation in Fig. 5-6, it showed that the photodegradation increased as the time increased conversely. Among 3 control experiments were TiDark, UVC and TiUVC, and the 3 systems of photodegradation at 120 min. were listed as 11.4%, 14.64 % and 18.93%, respectively. Based on the lowest TiDark system, UVC irradiation increased 3.2 % photodegradation. With the combination of TiO_2 +UVC, it also increased to 7.5%. This evidences clearly showed that UVC irradiation on TiO_2 photocatalyst [27], it generated OH for pyrocatechol photodegradation from e^-h^+ formation as Eq. (2). It argued that UVC was the important factor to photoactivation of e^-h^+ formation on the surface and provided energy band gap of 3.2 eV as it was enough for photo-excitation from valence band(VB) to conduction band(CB) [28]. Then, hydroxyl ion and H_2O

adsorbed species also interacted with h^+_{VB} to form OH radicals as Eq. (3)-(4). With O_2 adsorbed species from the diffusion, they also interacted with e^-_{CB} to generate OH in Eq. (5).

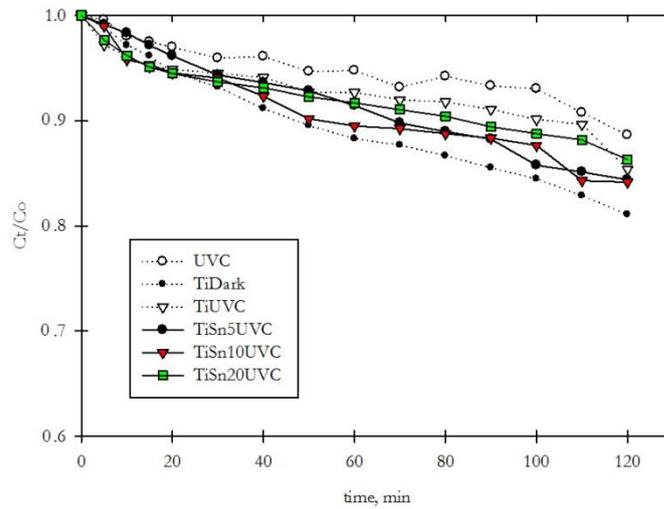
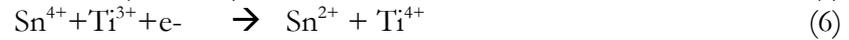
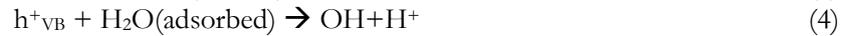


Fig. 5. The profile C_t/C_0 from various Sn/Ti ratio on $SnCl_2$ -doped TiO_2 photocatalyst. Each experiment was carried out by 1 g photocatalyst with 1 liter of 1mM pyrocatechol at room temperature.

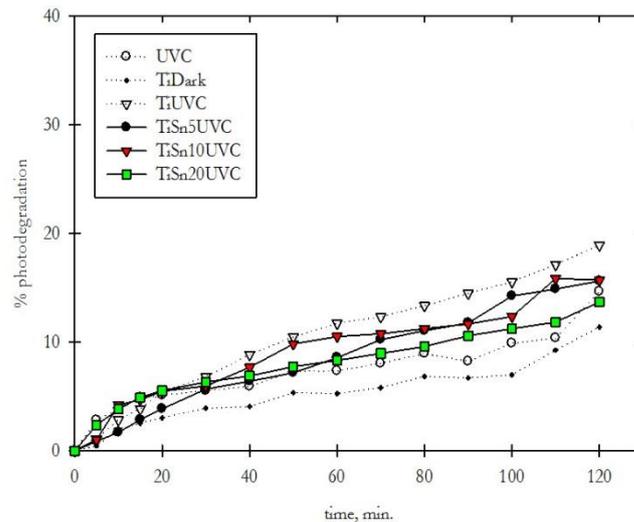


Fig. 6 Pyrocatechol photodegradation with UVC irradiation of $SnCl_2$ -doped TiO_2 photocatalyst without H_2O_2 .

The addition of Sn on TiO_2 photocatalyst, $SnCl_2$ -doping caused the order of photodegradation starting from 13.69% by $TiSn20UVC$, 15.62% by $TiSn5UVC$ and 15.71% by $TiSn10UVC$, respectively. The Sn/Ti ratio from 5% to 10% gave higher photodegradation than Sn/Ti =20%. This suggested that excessive $SnCl_2$ -doping inhibited the OH formation or suppressed pyrocatechol photodegradation. It pointed out that the presence of SnO_2 on the surface possibly generated OH indirectly by UVC irradiation but less than that from $TiUVC$ of 18.93% system. The optimal amount of $SnCl_2$ doping within 10% delayed e^- - h^+ recombination as those results found for V-doping and Fe-doping on TiO_2 photocatalyst [29]. Another reason from redox couple of Sn^{4+} and Ti^{3+} took place in Eq. (7). The higher photodegradation occurred with H_2O_2 addition in the next section.

3.2.2. Effect of H₂O₂+UVC irradiation on pyrocatechol photodegradation

There were 3 control experiments – HODark, HOUVC, and TiHOUVC in Fig. 7. As the time increased, the value of C_t/C_0 decreased monotonically. Using Eq. (1) to derive photodegradation, it was plotted in Fig. 8. They showed that the photodegradation became 15.63%, 25.0% and 26.5%, respectively. Comparison between HODark and HOUVC [30], the UVC irradiation increased about 10% photodegradation described by Eq. (7). The photolysis in Eq. (7), it gave more OH free radicals than HODark system did. But TiHOUVC and HOUVC had the slightly different of % photodegradation due to the same amount of OH formed, even the TiO₂ photocatalyst existed. Prior to the previous reports, the presence of H₂O₂ could increase photodegradation significantly on Sn(4+)/TiO₂ on Activated carbon for Orange G degradation to 91% [31]. In case of o-chloroaniline destruction, the addition of H₂O₂ in the proper amount, it increased the hydroxyl free radicals but the excess amount of H₂O₂ was avoided [32]. For 2-phenylphenol photo-transformation, it got the better performance with the small amount of H₂O₂ [33]. These indicated that the H₂O₂ was the important factor to increase the photodegradation activity. The clear evidence will be shown in the results.

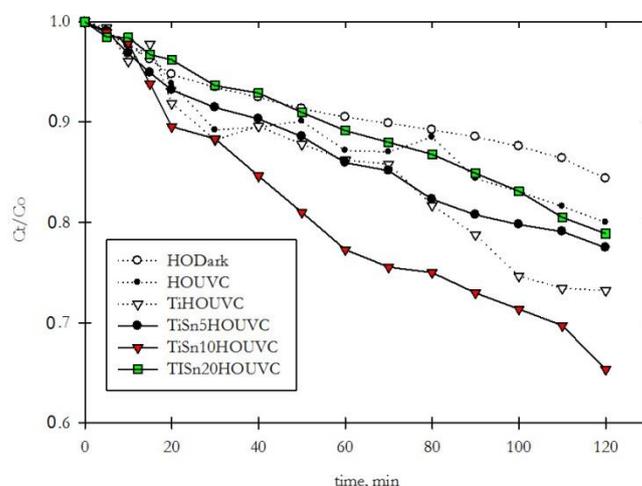
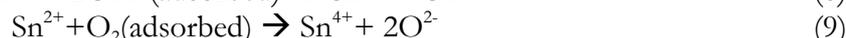
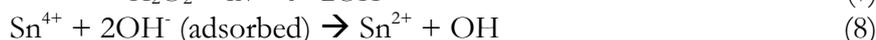


Fig.7. The profile of C_t/C_0 from H₂O₂ + UVC addition on SnCl₂-doping TiO₂ photocatalyst for pyrocatechol photodegradation. Each experiment was carried out by 1 g photocatalyst with 1 liter of 1mM pyrocatechol at room temperature. The symbol of HO represented the experiment with H₂O₂ addition.

Among all SnCl₂-doped TiO₂ photocatalyst, they showed the order of photodegradation as TiSn20HOUVC < TiSn5HOUVC < TiSn10HOUVC of 21.12% < 22.52% < 34.65%, respectively. The increase of Sn/Ti from 5 to 10, Sn/Ti of 10, it gave the highest photodegradation among the others. Whereas, at Sn/Ti = 20 was not the optimum amount because the excessive Sn increased the recombination [7, 29]. And its segregate particles formed in Fig. 3(d). Such the larger particles had screening effect for UVC irradiation on the active site during photodegradation. The interaction of SnO₂ on TiO₂ photocatalyst affected the photoactivity as listed in Eq. (6)-(9).



The previous experiment showed that Sn/Ti of 10 gave 34.65% of the highest photodegradation with H₂O₂+UV irradiation in Fig. (8). The chemical kinetic analysis of pyrocatechol photodegradation by SnCl₂-doped TiO₂ photocatalyst, it had the supporting results in Table 2. Most of the order of reaction, they followed 2nd order with the SnCl₂-doping, and rate constants increased significantly. Only UVC irradiation in Fig. (8), the increase of 5% to 20% SnCl₂-doping, it decreased the rate constant from 1.5x10⁻³ to 1.0x10⁻³ Liter/ (mole.s) significantly. It meant that excessive Sn doping suppressed the OH free radical formation and showed the adverse effect to photodegradation of pyrocatechol as well. The rate constant of TiSn5UVC,

TiSn10UVC and TiSn20UVC had 1.5×10^{-3} , 1.3×10^{-3} and 1.0×10^{-3} Liter/(mole.s), respectively. The supporting evidences from OHDark and TiDark showed 1.4×10^{-3} and 1.7×10^{-3} Liter/(mole.s) with low % photodegradation.

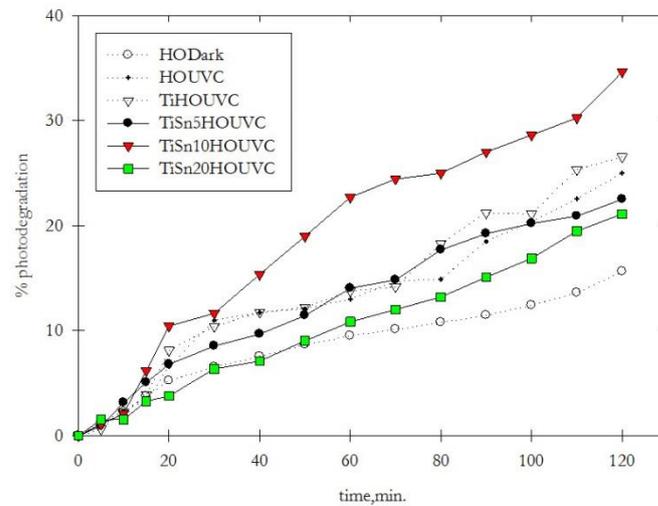


Fig. 8. Effect of H_2O_2 +UVC irradiation on pyrocatechol photodegradation by SnCl_2 -doped TiO_2 photocatalyst.

Table 2. Order of reaction and reaction rate constants for SnCl_2 -doped TiO_2 photocatalysts.

Title	Order of reaction	k
UVC	0	0.7×10^{-3}
TiUVC	0	0.7×10^{-3}
TiHOUVC	1	2.6×10^{-3}
HODark	2	1.4×10^{-3}
TiDark	2	1.7×10^{-3}
HOUVC	2	1.9×10^{-3}
TiSn5UVC	2	1.5×10^{-3}
TiSn5HOUVC	2	2.4×10^{-3}
TiSn10UVC	2	1.3×10^{-3}
TiSn10HOUVC	2	3.7×10^{-3}
TiSn20UVC	2	1.0×10^{-3}
TiSn20HOUVC	2	2.6×10^{-3}

On the other hand for H_2O_2 + UVC irradiation, TiSn5HOUVC to TiSn20HOUVC, the HOUVC testing with SnCl_2 -doping increased the rate constant from 2.4×10^{-3} to 3.7×10^{-3} Liter/(mole.s) in Table 2. It increased about 1.6 to 2.9 times compared to those of UVC and HOUVC. The presence of H_2O_2 increased the OH free radical and photo-reactivity for pyrocatechol photodegradation by Eq. (7) and it increased rate constants. To compare the effect of Sn-Cl₂ doping in Fig. 9, TiUVC had the rate constant of 0.7×10^{-3} the same as UVC in zero order. And TiHOUVC had the rate constant of $2.6 \times 10^{-3} \text{ s}^{-1}$ with 1st order which was not the same as TiUVC constant. The order changed from zero to 1st order due to H_2O_2 changed the photodegradation pathway. It meant that photocatalyst with 5%-20% Sn, HOUVC could activate the active sites on TiO_2 surface. Hence, it showed that the increase of rate constant with HOUVC photoactivation increasing of OH free radicals for the photodegradation. The presence H_2O_2 in the reaction increased the photoreactivity contributing from the increase OH radicals significantly. This followed the results of H_2O_2 influence [31-33]. The effect of SnCl_2 -doping did not change the photodegradation pathway on the surface of photocatalyst with reaction order changes, but it also

substituted TiO_2 lattice with narrowed the surface energy gap [34]. It involved the kinetics and the energy interaction. The FTIR method will clarify the adsorbed species in the further studies.

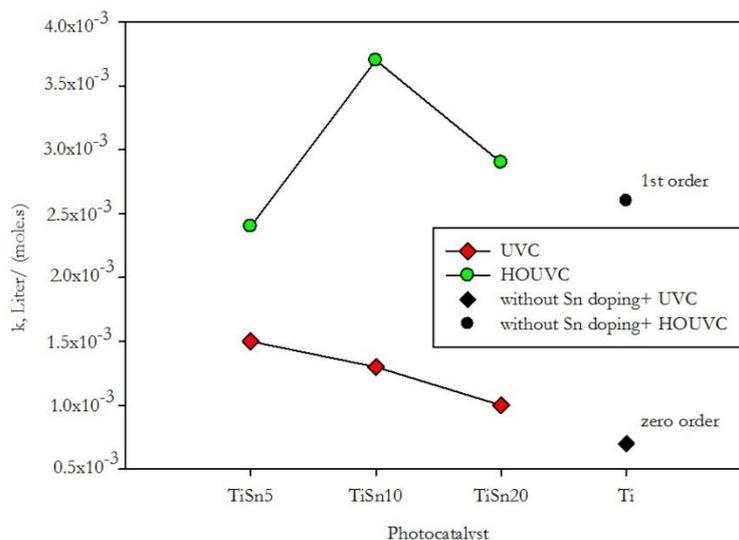


Fig. 9. The comparison of rate constant between % SnCl_2 -doping and UVC with HOUVC condition. The control experiment had the symbols of \blacklozenge representing for TiUVC and \bullet for TiOHUVC without SnCl_2 -doping.

4. Conclusion

SnCl_2 -doping on TiO_2 photocatalyst by impregnation, it generated SnO_2 as cassiterite located on TiO_2 bulk lattice as WAXD pattern. The SnCl_2 doping increased the particle agglomeration and it formed segregation at Sn/Ti of 20 from laser particle sizer due to the attraction force. Using SnCl_2 -doped TiO_2 photocatalyst for pyrocatechol photodegradation with UVC irradiation, it was found that the addition of Sn from 5% to 20% wt slightly increased the photodegradation about 3% to 7%. Meanwhile, the H_2O_2 +UVC condition, it enhanced significantly the pyrocatechol photodegradation to 34.65% for TiSn10HOUVC. This was the contribution of OH free radicals formation by SnCl_2 -doping and its interaction of e^-h^+ formation. Sn^{4+} and Ti^{4+} shared the same ion radius and lattice type so the redox reaction occurred easily.

Then, chemical kinetic analysis, TiSn10HOUVC showed the photodegradation reaction followed 2nd order and $k = 3.7 \times 10^{-3} \text{ l/ (mol.min)}$. They corresponded to the synergistic effect of OH free radicals' formation and they gave the higher activity of pyrocatechol photodegradation. The SnCl_2 -doping generated SnO_2 into the TiO_2 lattice and it affected the photodegradation with the increase of the reaction rate constant. This supported that the catalyst preparation governed catalyst properties to its photoreactivity. The ion size of Sn-Ti, redox reaction between the Sn-Ti enhanced the photodegradation reactivity. The further studied will examine on FTIR method of the SnCl_2 -doped TiO_2 photocatalysts to understand the adsorbed species on the surface.

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Reference

- [1] D. Sheddon, *Petrochemical Economics*. London, UK: Imperial College Press, 2010.
- [2] K. Weisser, *Industrial Organic Chemistry*, 2nd ed., New York, USA: VCH, 1993.
- [3] G. Busca, S. Berardinelli, C. Resini, and L. Arrighi, "Technologies for the removal of phenol from fluid streams: A short review of recent developments," *J. Hazardous Mat.*, vol. 160, pp. 265-288, 2008.

- [4] G. Lofrano, L. Rizzo, M. Grassi, and V. Belgiorno, "Advanced oxidation of catechol: A comparison among photocatalysis, Fenton and photo-Fenton processes," *Desalination*, vol. 240, pp. 878-883, 2009.
- [5] A. Fujishima and X. Zhang, "Titanium dioxide photocatalysis: Present situation and future approaches," *C. R. Chimie*, vol. 9, no. 5-6, pp. 750-760, 2006.
- [6] J. M. Herrmann, "Heterogeneous photocatalysis: State of art and present application," *Topics in Catalysis*, vol. 34, no. 1-4, pp. 49-65, 2005.
- [7] O. Carp, C. L. Huisman, and A. Reller, "Photoinduced reactivity of titanium dioxide," *Prog. Solid State Chem.*, vol. 32, pp. 33-177, 2004.
- [8] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, "Environmental application of Semiconductor photocatalysis," *Chem. Rev.*, vol. 95, pp. 69-96, 1995.
- [9] K. Garfield, and J. Potter, "System and method for photocatalytic air filtration using substrate with photocatalytic particle powder coated thereon," US7820100 B2, 26 Oct. 2007.
- [10] H. J. Kim, S. C. Lee, and J. B. Lee, "Method for preparing uniform anatase TiO₂ nanoparticle," US Patent 8357348 B2, 22 Jan. 2013.
- [11] J. Regalbuto, *Catalyst Preparation: Science and Engineering*. USA: CRC Press, 2007,
- [12] J. R. H. Ross, *Heterogeneous Catalysis*. Spain: Elsevier, 2012.
- [13] K. J. Klabunde and R. M. Richards, *Nanoscale Material in Chemistry*, 2nd ed. USA: John Wiley & Sons, Inc., 2009.
- [14] Y. Yalcin, M. Kilic, and Z. Cinar, "Fe³⁺-doped TiO₂: A combined experimental and computational approach to the evaluation of visible light activity," *Applied Cat. B.*, vol. 99, pp. 469-477, 2010.
- [15] M. Astilurk, F. Sayikan, and E. M. Arpac, "Effect of Fe³⁺ ion doping to TiO₂ on the photocatalytic degradation of malachite green dye under UV and vis-irradiation," *J. Photochem. Photobiol. A*, vol. 203, pp. 64-71, 2009.
- [16] X. Zhang, Y. Cao, S. Kan, Y. Chen, J. Tang, K. Jin, Y. Bai, L. Xiao, T. Li, and B. Li, "Study on the photo-induced interfacial charge transfer in TiO₂/Fe₂O₃ heterostructured composite film," *Thin Solid Film*, vol. 327-329, pp. 568-570, 1998.
- [17] A. M. T. Silva, C. G. Silva, G. Darzic, and J. L. Faria, "Ce-doped TiO₂ for photocatalytic degradation of chlorophenol," *Cat. Today*, vol. 144, no. 13-18, 2009.
- [18] L. Gomathi Devi, B. Narasinha Murthy, and S. Girish Kumar, "Photocatalytic activity of TiO₂ doped with Zn²⁺ and V⁵⁺ transition metal ions: Influence of crystallite size and dopant electronic configuration on photocatalytic activity," *Mat. Sci. Eng. B*, vol. 106, pp. 1-6, 2010.
- [19] H. Zhang, G. Chen, and D. W. Bahnemann, "Photocatalytic materials for environmental application," *J. Mater. Chem.*, vol. 19, pp. 5089-5121, 2009.
- [20] R. Sasikala, A. Shirole, V. Sudarsan, T. Sakumtala, C. Sadakar, R. Naik, and S. R. Bharawaj, "Highly dispersed phase of SnO₂ on TiO₂ nanoparticles synthesized by polyol-mediated route: Photocatalytic activity for hydrogen generation," *Int. J. Hydrogen Energy*, vol. 34, no. 9, pp. 3621-3630, 2009.
- [21] K. Lee, N. H. Lee, S. H. Shin, H. G. Lee, and S. J. Kim, "Hydrothermal synthesis and photocatalytic characterizations of transition metals doped nano TiO₂ sols," *Mater. Sci. & Engng. B*, vol. 129, no. 1-3, pp. 109-115, 2006.
- [22] S. H. Woo, W. W. Kim, S. J. Kim, and C. K. Rhee, "Photocatalytic behaviours of transition metal ion doped TiO₂ powder synthesized by mechanical alloying," *Mater. Sci. Engng. A*, vol. 499-451, pp. 1151-1154, 2007.
- [23] F. Sayikan, M. Asilturk, P. Tatar, N. Kiraz, S. Sener, E. Arpac, and H. Sayikan, "Photocatalytic performance of Sn-doped TiO₂ nanostructured thin film for photocatalytic degradation of malachite green dye under UV and VIS-lights," *Mat. Res. Bull.*, vol. 43, pp. 127-134, 2008.
- [24] M. Sahu, K. Suttipongparnit, S. Suvachittanont, T. Charinpanikul, and P. Biswas, "Characterization of doped TiO₂ nanoparticle dispersions," *Chem. Engng. Sci.*, vol. 66, no. 15, pp. 3482-3490, 2011.
- [25] K. Suttiponparnit, J. Jiang, M. Sahu, S. Suvachittanont, T. Charinpanitkul, and P. Biswas, "Role of surface area, primary particle size, and crystal phase on titanium dioxide nanoparticle dispersion properties," *Nanoscale Res. Lett.*, vol. 6, no. 27, 2011.
- [26] L. Gomathi, B. Narasimha Murthy, and S. G. Kumar, "Photocatalytic activity of TiO₂ doped with Zn²⁺ and V⁵⁺ transition metal ions: Influence of crystallite size and dopant electronic configuration on photocatalytic activity," *Mater. Sci. Engng. B*, vol. 166, no. 1-6, 2010.
- [27] A. Fujishima, X. Zhang, and D. A. Tryk, "TiO₂ photocatalysis and related surface phenomena," *Surf. Sci. Rep.*, vol. 63, pp. 515-582, 2008.

- [28] U. I. Gaya and A. H. Abdullah, "Heterogeneous photocatalytic degradation of organic contaminations over titanium dioxide: A review of fundamentals, progress and problems," *J. Photochem. Photobiol. C.*, vol. 9, no. 1-12, 2008.
- [29] M. A. Rauf, M. A. Meetani and S. Hisaindee, "A overview on the photocatalytic degradation of azo dyes in the presence of TiO₂ doped with selective transition metals," *Desalination*, vol. 270, pp. 13-27, 2011.
- [30] W. Z. Tang, *Physicochemical Treatment of Hazardous Wastes*. CRC press, USA, 2004.
- [31] J. H. Sun and X. L. Wang, "Photocatalytic degradation and kinetics of Orange G using nano-sized Sn(IV)/TiO₂/AC photocatalyst," *J. Mol. Cat. A*, vol. 260, no. 1-2, pp. 241-246, 2006.
- [32] W. K. Choy and W. Chu, "Destruction of o-Chloroaniline in UV/TiO₂ Reaction with Photosensitizing Additives," *Ind. Eng. Chem. Res.*, vol. 44, no. 22, pp. 8184-8189, 2005.
- [33] A. A. Khodja and T. Sehili, "Photocatalytic degradation of 2-phenylphenol on TiO₂ and ZnO in aqueous suspensions," *J. Photochem. Photobiol. A*, vol. 141, no. 2-3, pp. 231-239, 2001.
- [34] H. Yang and Q. Tao, "Preparation and Characterization of Doped Titanium dioxide thin films," *Opt. Adv. Mater. Rapid Comm.*, vol. 2, no. 12, pp. 806-810, 2008.