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Bulletin of Chemical Reaction Engineering & Catalysis, 12 (3), 2017, 430-436

Research Article

The Role of Concentration Ratio of TTiP:AcAc on the Photocatalytic Activity of TiO_2 Thin Film in Reducing Degradation Products of Used Frying Oil

Ummi Kaltsum[1]*, Affandi Faisal Kurniawan[1], Iis Nurhasanah[2], P. Priyono[2]

[1]Physics Education Department, Universitas PGRI Semarang, Jl. Sidodadi Timur No.24, Semarang 50125, Indonesia
[2]Physics Department, Universitas Diponegoro, Jl. Prof. Soedarto, Kampus Undip Tembalang, Semarang 50275, Indonesia

Received: 20th February 2017; Revised: 27th May 2017; Accepted: 30st May 2017; Available online: 27th October 2017; Published regularly: December 2017

Abstract

The TiO_2 thin film has been applied to reduce degradation products (free fatty acid/FFA and peroxide value/PV) in used frying oil under ultraviolet (UV) light irradiation. FFA and PV are degradation products in used frying oil that can cause various diseases in human. In this study, the TiO_2 thin films were made from precursor solution with concentration ratio of titanium tetraisopropoxide (TTiP) and acetylacetone (AcAc) of 1:1, 1:2, 2:1, 2:3, and 3:2. The aim of this study is to investigate the effect of concentration ratio of TTiP and AcAc on the photocatalytic activity of TiO_2 thin film in reducing FFA and PV of used frying oil. The spray coating method was used to deposit precursor solution of TiO_2 onto glass substrate at 450 °C. All TiO_2 thin films consist of spherical-like grain with dominant structure of TiO_2 rutile. The band gap energy of TiO_2 thin films was in the range 3.11-3.16 eV. Concentration ratio of TTiP and AcAc of 2:3 results in TiO_2 thin film with highest photocatalytic activity in reducing FFA and PV of used frying oil.

Keywords: TiO_2 thin film; TTiP; AcAc; Used frying oil; Photocatalytic activity

How to Cite: Kaltsum, U., Kurniawan, A.F., Nurhasanah, I., Priyono, P. (2017). The Role of Concentration Ratio of TTiP:AcAc on the Photocatalytic Activity of TiO_2 Thin Film in Reducing Degradation Products of Used Frying Oil. *Bulletin of Chemical Reaction Engineering & Catalysis*, 12 (3): 430-436 (doi:10.9767/bcrec.12.3.951.430-436)

Permalink/DOI: https://doi.org/10.9767/bcrec.12.3.951.430-436

1. Introduction

Titanium dioxide (TiO_2) has interesting properties, i.e. high brightness, very high refractive index, and strong UV light absorption [1]. Therefore, the TiO_2 has been widely used as white pigment, sunscreen, and photocatalyst. Under UV light irradiation, TiO_2 has strong photocatalytic activity. As a photocatalyst, TiO_2 has been applied in many fields, especially for pollutant photodegradation. Ioana and Moldovan reported the photodegradation of the indoor organic pollutant (toluene and chlorobenzene compounds) in the air [2]. Photodegradation of nitrogen oxides, odorous compounds, fungi, etc. in the air was studied by Miller and Fox [3]. In addition, photodegradation of pathogenic microorganisms [4] and different dyes (methylene blue and congo red) in the water were also reported [5].

Free fatty acid (FFA) and peroxide value (PV) are degradation products in frying oil pro-

* Corresponding Author.
E-mail: ummikaltsum@upgris.ac.id (Kaltsum, U.)
Telp.: +62-24-8316377; Fax.: +62-24-8448217

duced during frying process. FFA and PV are degradation products that produced by frying process and used to monitor quality of frying oil [6-9]. These molecules cause extreme human health problems, cancer and heart coronary disease [10-13]. The common method in reducing FFA and PV is filtration using adsorbent [14-16]. However, this method need long process and a lot of equipment. The other methods to reduce FFA and PV are the using of acid catalyst [17-19] and adding antioxidant [20,21].

Recently, TiO_2 in the form of thin film has been used as an alternative technology in reducing free fatty acid (FFA) and peroxide value in used frying oil as a simple process and equipment [22,23]. Kaltsum *et al.* [22] used TiO_2 thin film to reduce FFA and PV in used frying oil under sunlight and UV light irradiation for 5 hours. The precursor solution of TiO_2 thin film was mixture of Titanium Tetraisopropoxide (TTiP) 0.2 M, Acetylacetone (AcAc) 0.4 M, and ethanol was deposited by spray coating method. The result showed that the TiO_2 thin film could reduce FFA and PV up to 67.10 % and 79.15 % in used frying oil, respectively .

Comparison of reduction FFA and PV using sunlight and UV light irradiation was also analyzed by Kaltsum *et al.* [23]. Under sunlight irradiation, the TiO_2 thin film was able to reduce FFA and PV up to 49.09 % and 20.96 %, respectively. On the other hand, under UV light irradiation, TiO_2 thin film reduced FFA and PV up to 61.81 % and 53.22 %, respectively. Therefore, UV light irradiation was more effective in reducing FFA and PV than sunlight irradiation. Oja *et al.* [24] used TiO_2 thin film made of TTiP and AcAc with concentration ratio of 2:1 for structural and electrical characterization.

In this study, concentration ratio of TTiP and AcAc in precursor solution of TiO_2 thin film is varied into five ratios and the thin film used to purify used frying oil. The aim of this study is to investigate the effect of concentration ratio of TTiP and AcAc on the photocatalytic activity of TiO_2 thin film to purify used frying oil under UV light irradiation. The parameter of percent FFA and PV are used to monitor the quality of used frying oil.

2. Materials and Methods

2.1 Manufacture of thin film

The material and procedure used in this research was based on the material and procedure as describe in the previous research [1,2]. The TiO_2 thin film was made by spraying precursor solution onto glass substrate at temperature 450 ^{o}C. The precursor solution was made by mixing TTiP (97 %, Sigma-Aldrich, AcAc (99 %, Merck KgaA, and absolute ethanol (Merck KgaA). The concentration ratio of TTiP:AcAc was varied into 5 conditions. They were 1:1, 1:2, 2:1, 2:3, and 3:2, respectively.

2.2 TiO_2 thin film characterization

The properties of TiO_2 thin films were characterized using JEOL JSM-6510 LA Scanning Electron Microscope (SEM), Shimadzu 1240 UV-visible spectrophotometer, and MAXima_X XRD-7000X-ray diffractometer. The thickness of TiO_2 thin films was estimated using SEM image and the result as shown in Table 1. The XRD pattern was used to analyze structure and crystallite size of TiO_2 thin films. The optical properties of TiO_2 thin films were analyzed through absorbance spectra in the range 200-800 nm.

2.3 Determination of FFA and PV

Reduction of FFA and PV in used frying oil was carried out by putting TiO_2 thin in used frying oil and irradiated by UV light for 5 hours. The FFA and PV of used frying oil before and after irradiation were determined by titration method of AOCS [25,26]. Ten gram used frying oil was added to 50 mL hot ethanol and 5 drops of phenolphthalein. The mixture was titrated with 0.1 N KOH by shaking until a light pink color appeared. The value of FFA was determined using equation (1).

$$\% FFA = \frac{56.1\, NV}{W} \quad (1)$$

where, N is the normality of KOH, V is the volume of KOH (mL), and W is the mass of used frying oil (g).

Five gram used frying oil was added to 50 mL acetate acid and shaked until the mixture homogeneous. 0.5 mL KI and 30 mL distilled water were added to that the mixture and shaked for 1 minute, respectively. The mixture was titrated by 0.1 N $Na_2O_3S_2$ until the yellow color disappear. 0.5 mL amilum liquid was added to mixture. The titration was continued until the blue color disappear. The peroxide value was determined using equation (2).

$$PV = \frac{1000\, NV}{W} \quad (2)$$

where N is the normality of $Na_2O_3S_2$, V is the volume of $Na_2O_3S_2$ (in mL), and W is the mass of used frying oil (in grams).

3. Results and Discussion

3.1 Properties of TiO_2 thin film

3.1.1 Structure and morphology

The structure of TiO_2 thin films was analyzed by XRD patterns as shown in Figure 1. It can be seen that all TiO_2 thin films have the same pattern with three strong peaks at 2θ of 44°, 64°, and 77°, respectively. By comparing with JCPDS No. 21-1276 and No. 16-0617, the three strong peaks corresponded to the (210) and (310) plane of rutile TiO_2, and (024) plane of brookite TiO_2, respectively. However, a small peak was also observed at 2θ = 37° for thin film with TTip:AcAc ratio of 1:1, 1:2, 2:1, and 2:3 which correspond to the (004) plane of anatase (JCPDS No. 21-1272). This result indicates that TiO_2 thin film was formed by a mixture of rutile, brookite, and anatase structure which rutile as predominant structure. The crystallite size of TiO_2 thin films was calculated using equation (3) for strongest diffraction peak of rutile (210) [27].

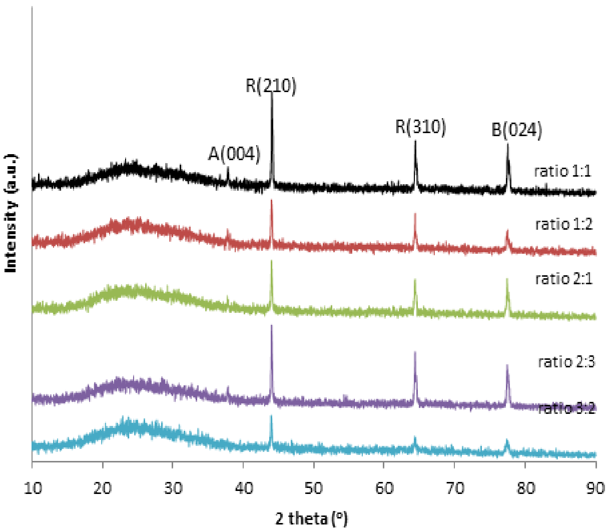

Figure 1. The XRD pattern of five TiO_2 thin films

Table 1. The mean crystallite size and the thick-

No	TTiP:AcAc ratio	Mean crystallite size (nm)	Thickness (μm)
1	1:1	49.86	0.719
2	1:2	42.73	0.915
3	2:1	53.41	0.288
4	2:3	59.83	1.569
5	3:2	53.42	0.651

$$D = \frac{0.9\,\lambda}{\beta\, cos\,\theta} \qquad (3)$$

where D is crystallite size, λ is X-ray wavelength, β is full width at half of maximum, and θ is Bragg's angle. Table 1 shows the crystallite size of TiO_2 thin film. It can be found that the crystallite size of TiO_2 thin film with ratio 2:3 was the largest, 59.83 nm.

The surface morphology of TiO_2 thin films was characterized by SEM as shown in Figure 2. The surfaces of all TiO_2 thin films consist of spherical like-grains.

3.1.2 Optical properties

The absorbance spectrums of all TiO_2 thin films were investigated by UV VIS spectrophotometer as depicted in Figure 3. All TiO_2 thin films show strong absorption at ultra violet range of 290-400 nm and low absorption at visible light range of 400-800 nm. Therefore, the high photocatalytic activity of TiO_2 thin films can be obtained by using UV light as a radiation source.

In spite of being the same material, the absorbance of each thin film in Figure 3 is different each other. It is due to each thin film has a different rutile, brookite, and anatase phase composition and different thickness. The high thickness leads more light absorbed, so it increases absorbance. The same result also was reported by Samoom *et al.* [28] that increasing of thickness increased absorbance. The strong UV absorbtion obtained for TiO_2 thin film deposited at TTiP:AcAc ratio of 1:2 and 2:3.

The absorbance data that can be used to determine energy gap of thin film by Tauc plot method based on the Equation for indirect transition (Equation 4) [29] and the result is listed in Table 2. The indirect band gap of rutile TiO_2 was 3.10 eV as reported by Welte and Monllor [30,31].

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \qquad (4)$$

where a is absorption coefficient, $h\nu$ is photon energy, A is constant, and E_g is band gap energy.

The band gap energy of TiO_2 thin films are in the range 3.11-3.16 eV. The highest band gap energy is shown by TiO_2 thin film with ratio 1:2. On the contrary, the lowest band gap energy was shown by TiO_2 thin film with ratio 1:1.

3.2 Photocatalytic properties of TiO_2 thin films

In this research, photocatalytic properties of TiO_2 thin films is applied to reduce FFA and PV in used frying oil. The photocatalytic process in TiO_2 thin film can be explained in three steps. First, when the UV light (photon) irradiates thin film, electron in valence band excites to conduction band and produce hole and conduction electron as shown in Equation (5) [32]. Second, hole and conduction electron react with carboxylic acid (main component of frying oil) produce hydrocarbon radical and hydrogen radical as shown in Equations (5-7), respectively [33]. The last, both radical react with degradation products (FFA and oxidation products), so the percentage of FFA and PV reduced.

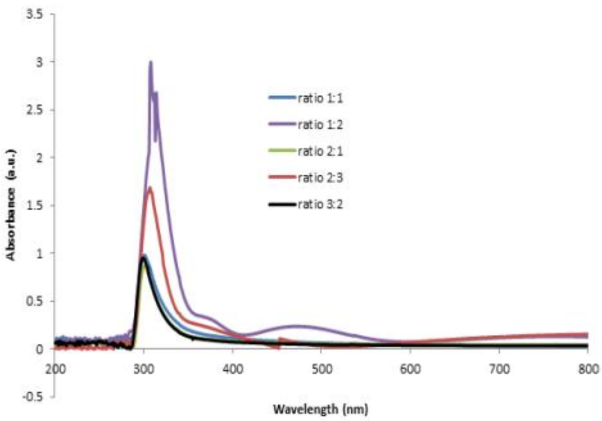

Figure 3. The absorbance spectrum of TiO_2 thin films for various TTiP:AcAc ratio

$$TiO_2 + h\nu \text{ (photon)} \rightarrow e_{cb}^- + h_{vb}^+ \quad (5)$$
$$RCO_2^- + h_{vb}^+ \rightarrow R\bullet + CO_2 \quad (6)$$
$$RCOOH + e_{cb}^- \rightarrow H\bullet + RCO_2^- \quad (7)$$

The photocatalytic activities of the thin film in used frying oil were evaluated via the reduction of degradation products (FFA and PV) under UV light irradiation. Reduction of FFA and PV can be determined using Equation (8) and (9), respectively.

$$R(of\ FFA) = \frac{FFA_i - FFA_f}{FFA_i} x100\% \quad (8)$$

Table 2. The band gap energy of five TiO_2 thin films

No	TiO_2 thin film	Indirect (eV)
1	Ratio of 1:1	3.11
2	Ratio of 1:2	3.16
3	Ratio of 2:1	3.15
4	Ratio of 2:3	3.12
5	Ratio of 3:2	3.13

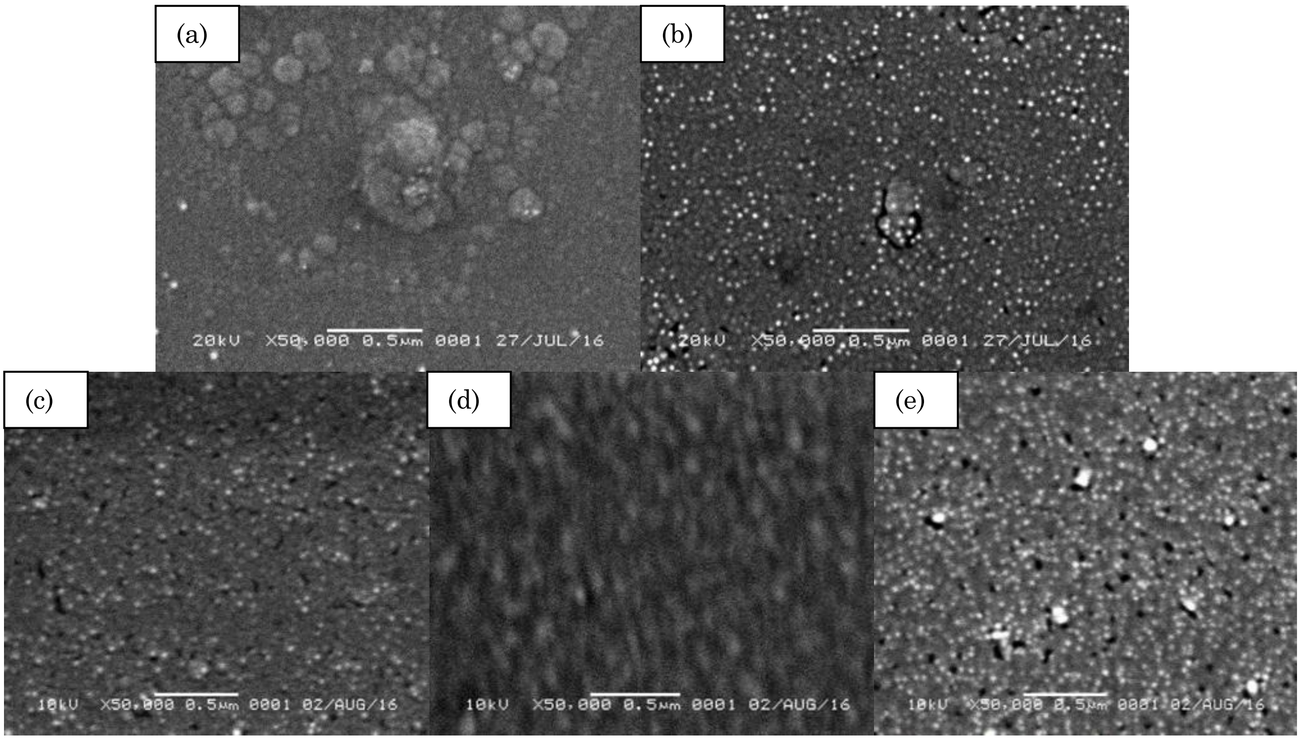

Figure 2. SEM image of TiO_2 thin film with concentration of TTiP and AcAC with ratio (a) 1:1, (b) 1:2, (c) 2:1, (d) 2:3, and (e) 3:2

$$R(of\ PV) = \frac{PV_i - PV_f}{PV_i} x100\% \quad (9)$$

where R is reduction (in %), FFA_i is initial value of FFA (in %), FFA_f is final value of FFA (in %), PV_i is initial value of PV (in meq/kg), and PV_f is final value of PV (in meq/kg). The results were shown in Figures 4-5.

The photocatalytic activity of thin film is affected by the absorbance, band gap energy, surface area, thickness [14,34], and annealing temperature [35,36]. The large absorbance means the large intensity of light adsorbed by thin film, so the high photocatalytic process occured. The smaller band gap energy, the more electron can be excited by photon to be conduction electron. The larger surface area, the more interaction between thin film and molecule of sample. Increasing thickness film leads increasing in surface area, so increasing contact between thin film and molecule of sample [34]. Increasing the number of conduction electron and interaction or contact between thin film and molecule increase the photocatalytic activities. In this research, the molecule meant is carboxylic acid as the main component of frying oil. The high photocatalytic activities refer to the high FFA and PVreduction in used frying oil.

The high reduction both of FFA and PV in used frying oil was shown by TiO_2 thin film with ratio 2:3. This might be mainly affected by the high thickness, large absorbance and small band gap energy of TiO_2 thin film with ratio 2:3. Effective reduction of FFA and PV is also observed in TiO_2 thin film with ratio 1:2 and 2:1, respectively. However, thin film with ratio 1:1 and 3:2 reduced small FFA and PV because of big band gap energy, low absorbance, and small thickness.

Addamo *et al.* [37] used three TiO_2 thin films (pure rutile, pure anatase, and pure brookite) to reduce 2-propanol. The result showed that pure brookite and pure anatase had better photocatalytic activity than pure-rutile. In this study, all the TiO_2 thin films have predominant rutile structure. However, they have high photocatalytic activity. It might be due to affected by the thickness, absorbance, and small band gap of thin film. In addition, rutile phase has the highest ultraviolet absortivity among the titanium dioxide phases, so it has high photocatalytic activity [38].

4. Conclusions

The TiO_2 thin films deposited at various concentration ratio of TTiP and AcAc have TiO_2 rutile predominant structure. The surface morphology of thin films was spherical-like grain. The band gap energy was around 3.11-3.16 eV. The TiO_2 thin films reduced FFA and PV up to 70.90 % and 58.54 % under UV light irradiation for 5 hours. The TiO_2 thin film with TTiP:AcAc concentration ratio of 2:3 posses the highest photocatalytic activity and the most effective in reducing FFA and PV of used frying oil.

Acknowledgement

This research was financial supported by ministry of Research, Technology, and Higher Education of The Republic of Indonesia with the research scheme of *Pekerti* in 2016.

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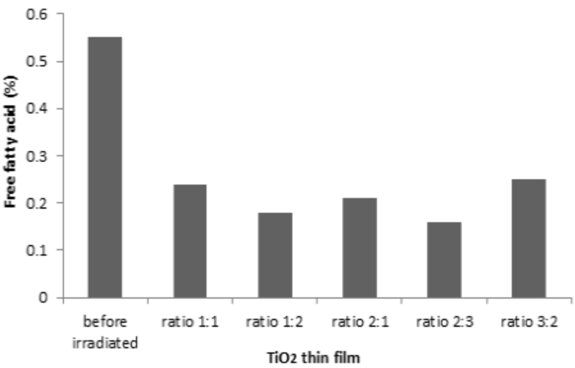

Figure 4. The percentage of FFA before and after photocatalysis process using TiO_2 thin film under UV light irradiation

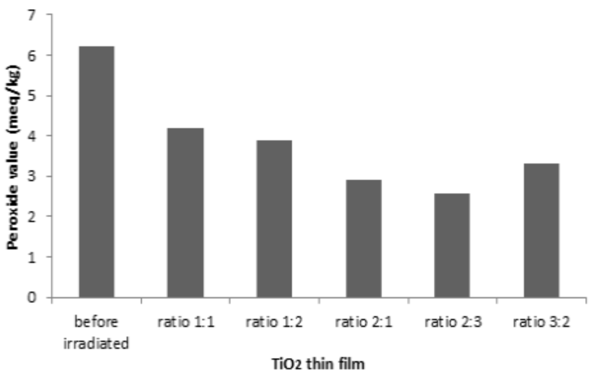

Figure 5. The percentage of PV before and after photocatalysis process using TiO_2 thin film under UV light irradiation

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