The Influence of Fe₂O₃ Addition on the TiO₂ Structure and Photoactivity Properties

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Abstract. The influence of Fe₂O₃ addition on the TiO₂ structure and photoactivity properties have been studied. The addition of Fe₂O₃ on the TiO₂ done by TiO₂-Fe₂O₃ synthesized with variation of annealing temperature. The result showed that peak of anatase TiO₂ at 2θ = 25.35° and Fe₂O₃ at 2θ = 54.20°. The XRD of TiO₂ show annealing temperature at 400°C is anatase phase and the composite with annealing at temperature 150°C, 300°C, 400°C and 500°C is crystalline anatase phase, due to the addition of Fe₂O₃. Photodegradation of Rhodamin B with TiO₂ at 400°C annealing temperature showed optimum degradation 36.2 %, and the composite with annealing at 400°C showed optimum degradation 44.3% for 300 minutes irradiation.

1. Introduction

Titanium dioxide (TiO₂) is a semiconductors that have photocatalytic activity. TiO₂ has three distinct crystalline structures i.e. anatase, rutile, and brookite. The synthesis of TiO₂ has been widely studied, Yan (2005) have prepared TiO₂ using TiCl₄ [1], Libanori (2009) performed TiO₂ using Titanium Tetraisopropoxide (TTIP) precursor by sol-gel technique [2], Lu (2010) synthesized TiO₂ using TTIP precursors [3], Wahyuningsih (2007) synthesized TiO₂ with TTIP sol gel method [4]. Among the frequently used methods for the synthesis of TiO₂, the sol-gel technique is an easy preparation than others. TiO₂ anatase has a good photocatalytic activity for the degradation of various organic compounds, including dyes. However, TiO₂ anatase can be irreversibly transformed into rutile in high temperatures. Therefore, the modified TiO₂ in order to form stable TiO₂ is required.

The modifications to form stable TiO₂ is addition of metal oxide into the molecule TiO₂ known as doping. The addition of dopant aims to inhibit the formation of rutile at high temperatures. According to Rao (1959) the presence of impurities (dopant) inhibits anatase-rutile transformation [5]. The presence of the dopant can increase the activity and catalytic efficiency of TiO₂. The performance of dopant can increase the uptake of TiO₂ in the visible region, thus enhancing the photocatalytic. Some types of metal oxides such as Fe₂O₃, CuO, and MnO₂ can be used as dopants. Riyas (2002) has study of comparing two different methods of co-precipitation and wet-impregnation in the synthesis of TiO₂ with Fe₂O₃ addition. The result indicated that Fe₂O₃ can affect the transformation of TiO₂ and obtained rutile crystal structure by co-precipitation method, and anatase crystalline structure with wet-
impregnation method at temperature 700°C and 900°C [6]. Music (2004) explained the transformation of β-FeOH to α- Fe₂O₃ began at temperature of 300°C and formed α- Fe₂O₃ crystalline phase at temperature of 400°C [7].

In this research, the synthesizes of TiO₂ and addition of Fe₂O₃ to know the change of crystal structure of TiO₂. The addition of Fe₂O₃ in variation of temperature can maintain the stability of TiO₂ crystal structure in anatase phase to increase the photocatalytic activity, which is used to degradation of Rhodamin B.

2. Experimental

2.1. Synthesis of TiO₂

CH₃COOH 98.5% (pH=2) was added 10 mL TTIP solution in water bath at ±10°-15°C till formed white solution. The mixture was stirred for 30 minutes formed transparent solution. The solution was heated at ±90°C to reduce CH₃COOH until sol gel form. The sol gel was heated at 150°C overnight and formed white TiO₂ powder. Then the TiO₂ was annealed at various temperature i.e. 150°C, 300°C, 400°C, 500°C, 600°C dan 700°C for 4 hours [4].

2.2. Synthesis of TiO₂-Fe₂O₃ composites

Fe(NO₃)₃.9H₂O 5.05 gram was added 25 ml aquadest and stirred until homogeneous. The mixture was added 11.45 g TiO₂ and stirred for an hours to orange colour. Then the sample was heated at 110°C overnight and obtained reddish-brown TiO₂-Fe₂O₃ composites. The composites of TiO₂-Fe₂O₃ was annealed at 150°C, 300°C, 400°C, 500°C, 600°C, 700°C and characterized by X-Ray diffraction (XRD), Fourier Transform Infrared and UV-Vis spectrophotometer.

2.3. Photodegradation of Rhodamin B with composites of TiO₂-Fe₂O₃ at various of annealing and time irradiation

The composites of TiO₂-Fe₂O₃ at temperature annealing of 150°C, 300°C, 400°C, 500°C, 600°C and 700°C were added 25 mL Rhodamin B (5 ppm), respectively. The solution was irradiated into black box for 0, 15, 30, 120, and 300 minutes. Then, the solution was filtered and the filtrate was characterized by UV-Vis spectrophotometer.
3. Results and Discussion

Figure 1. X-Ray Diffractogram of TiO$_2$ and TiO$_2$-Fe$_2$O$_3$ composites at annealing of 150°C ( ), 300°C ( ), 400°C ( ), 500°C ( ), 600°C ( ), and 700°C ( ).

X-Ray diffractogram of TiO$_2$ are shown in Figure 1. The synthesis of TiO$_2$ annealing at 150 °C and 300 °C were obtained the amorphous peaks which indicated the crystalline of TiO$_2$ was formed yet, while TiO$_2$ at 400°C, 500°C, 600°C, and 700°C have formed peaks of TiO$_2$ anatase at 2θ=25.35(d$_{101}=3.509$Å) according to JCPDS No. 78-2486 and new peaks appear at 2θ=27.50(d$_{110}=3.239$Å) that indicated the rutile phase according to JCPDS No. 87-0920. The ratio between anatase and rutile phase of TiO$_2$ (A:R) at various annealing are shown in Figure 2 and Table 1.

| Table 1. Ratio of Anatase/Rutile at various annealing |
|------------------------------------------------------|
| **Ratio** | **Annealing of TiO$_2$** |
| A:R       | 400°C | 500°C | 600°C | 700°C |
| 1:0.0     | 01:0.1| 01:0.7| 01:9.9 |
Figure 2. Ratio of Anatase/Rutile at various annealing

X-Ray diffractogram of TiO$_2$-Fe$_2$O$_3$ composites are shown in Figure 1 (strip line). TiO$_2$-Fe$_2$O$_3$ composites that annealed at 150°C and 300°C was obtained peaks of TiO$_2$ anatase at $2\theta = 25^0$ ($d_{101} = 3.537\text{Å}$) according to JCPDS No.78-2486, Fe$_2$O$_3$ at $2\theta = 53.90$ ($d_{116} = 1.699\text{Å}$) according to JCPDS No.87-1165, and appear peak of FeOH at $2\theta = 47.65$ ($d_{041} = 1.906\text{Å}$) according to JCPDS No.81-0462.

The synthesis of TiO$_2$ that annealed at 150°C and 300°C were formed amorphous phase, whereas after TiO$_2$-Fe$_2$O$_3$ composites formed a sharp peak indicating crystalline TiO$_2$. The presence of Fe$_2$O$_3$ dopant capable accelerates the formation of TiO$_2$ at low temperature. The TiO$_2$-Fe$_2$O$_3$ composites with annealing at 500°C indicated the dominant peak of the anatase phase at $2\theta = 25.35$ ($d_{101} = 3.509\text{Å}$), the dominant peak of Fe$_2$O$_3$ at $2\theta = 48.05$ ($d_{230} = 1.891\text{Å}$), $2\theta = 54.95$ ($d_{060} = 1.669\text{Å}$) and not formed yet the rutile phase in TiO$_2$ due to Fe$_2$O$_3$ dopant at 500°C this can resist the transformation TiO$_2$ anatase to rutile.

| Table 2. Degradation percentage (%) of Rhodamin B at various annealing temperatures and time irradiation |
|---------------------------------------------------------------|
| Degradation percentage (%) of Rhodamin B at various time irradiation |
| Variation annealing of TiO$_2$-Fe$_2$O$_3$ composites | 0 minutes | 15 minutes | 30 minutes | 120 minutes | 300 minutes |
|---------------------------------------------------------------|
| 150 | 0 | 3.2 | 5.0 | 10.9 | 17.6 |
| 300 | 0 | 1.3 | 3.1 | 7.2 | 24.8 |
| 400 | 0 | 0.0 | 5.4 | 16.2 | 44.3 |
| 500 | 0 | 0.0 | 3.0 | 7.5 | 23.5 |
| 600 | 0 | 0.0 | 5.1 | 12.5 | 13.9 |
| 700 | 0 | 5.2 | 8.1 | 8.2 | 9.8 |

The degradation curve ($A/A_0$ vs the variation of irradiation times) indicated that the longer time of irradiation can increase of degradation activity. The TiO$_2$-Fe$_2$O$_3$ composite that annealed at 400°C has high degradation (44.3%) compared with other temperature at 300 minutes irradiation due to the structure of TiO$_2$-Fe$_2$O$_3$ composite has a high percentage of anatase and hematite structure. TiO$_2$-
Fe$_2$O$_3$ composite that annealed at 500°C, 600 °C, and 700 °C with 300 minutes irradiation, the percentage of degradation decrease due to the presence of anatase-hematite structure decreases while rutile phase has been established. Thus the presence of Fe$_2$O$_3$ dopant into TiO$_2$ increases the photocatalytic activity to high irradiance time and inhibits the formation of rutile phases at high temperatures.

4. Conclusion
The influence of Fe$_2$O$_3$ addition on the TiO$_2$ structure and photoactivity properties has been studied. The TiO$_2$-Fe$_2$O$_3$ composite with annealed at 400°C has high degradation (44.3%) compared with other temperature at 300 minutes irradiation. And the TiO$_2$-Fe$_2$O$_3$ composite with annealed at 500°C, 600 °C, and 700 °C showed decrease of the percentage of degradation because decreases of the presence of anatase-hematite structure and rutile phase has been formed.

References
[1] Yan M F, Cheng J, Zhang J, and Anpo M 2005 J. Phys. Chem. B 109 8673-8678.
[2] Libanori R, Tania R G, Elson L, Edson R L, and Caue R 2009 J. Sol Gel Sci. Tech. 49 95-100.
[3] Luu C L, Quoc T N, and Si Thoang Ho 2010 Adv. Nat. Sci: Nanosci. Nanotech 1 1-5.
[4] Wahyuningsih S, Narsito, and Kartini L 2007 International Conference on Chemical Science Yogyakarta.
[5] Rao C and Turner 1959 J. Phys. Chem. Solids 11 173-175
[6] Riyas S, Yasir A, and Mohan D 2002 J. Bull. Mater. Sci. 25 267-273
[7] Music S, Krehula S, Propovic S 2004 Material Lettres 58 444-448