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Research Article

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The effect of the calcinations temperature during synthesis of TiO_2-Fe_3O_4-bentonite as photocatalyst material

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ABSTRACT

The TiO_2-Fe_3O_4 supported bentonite has been synthesized. The syntheses of the TiO_2-Fe_3O_4 based photocatalyst have been carried out by sol-gel method. The bentonite used for porous support was obtained from Pacitan, Indonesia. The mol ratio of Ti and Fe in this experiment was 1:1. The syntheses of the photocatalyst material were followed by calcinations. This experiment was focused on the effect of temperature calcinations toward Ti and Fe crystal phase, which was affected to the capability of the materials in photocatalysis of phenol degradation. The variation of the calcinations temperature was 500, 600 and 700°C. The physicochemical properties of TiO_2-Fe_3O_4 bentonite samples were characterized by X-ray diffraction. Photocatalytic activity of the materials was evaluated by phenol photodegradation using UV light. The calcinations temperature was significantly influenced in the forming of anatase phase of TiO_2 which was affected in the catalytic activity.

Keywords: bentonite; calcination; TiO_2-Fe_3O_4; phenol degradation; photocatalyst

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INTRODUCTION

Photocatalytic technology has various applications in degradation of organic and inorganic pollutants. Some of photocatalysts that have been used were TiO_2, Fe_2O_3 and other substances. TiO_2 has been widely used as photocatalysts because of its relatively high photocatalytic activity, biological and chemical stability, low cost, non-toxicity, and long term stability against photocorrosion and chemical corrosion [1,2]. However, TiO_2 has limitation on the aspect of the photocatalytic activity in the UV region and also the difficulty to be separated from the system. Some methods has been developed by the researchers to solve this limitations, such as doping transition metals [3,4,5,6], doping non-metallic elements [7,8,9,10,11], etc. Its purposes to enhance the photocatalytic activity of TiO_2 and also to improve the utilization of visible light. The researches resulted that the composite photocatalysts had higher photocatalytic activity than single ones. Therefore, iron oxide / iron ore (Fe_2O_3) can be added to TiO_2 as a stabilizer in the application of TiO_2. The existence of magnetite (Fe_3O_4) as a doping oxide in this composite also serves as a crystal formation controller of anatase phase. Anatase phase of TiO_2 photocatalyst give greater photocatalytic ability than the rutile phase of it [12]. In this study, it also used bentonite as a support catalyst. Bentonite generally is used as adsorbents and catalysts because of the pore number. The utilization of bentonite as solid support will facilitate and accelerate the mass transfer of adsorbate into the bentonite so that the contact between metal oxide of photocatalyst with organic compounds will more easily occur and react.

In this research, TiO_2/Fe_3O_4 photocatalyst were supported by bentonite. TiO_2/Fe3O4-bentonite photocatalytic material were prepared by sol gel method. The photocatalysts material were characterized by X-ray powder difraction (XRD). The photocatalytic activity of photocatalysts was evaluated by photocatalytic degradation of phenol compounds. The effect of calcination temperature on the photocatalytic activity of the TiO_2/Fe_3O_4-Bentonite were also discused.

EXPERIMENTAL SECTION

The selected metal salts, ammonium hydroxide, tetra methyl ammmonium hydroxe and ethanol were purchased from Sigma-Aldrich. Bentonite was obtained from Pacitan, Indonesia and size particle reduced up to 200 mesh. Nitrogen and Oxigen gases were purchased from Samator, Indonesia.

Preparation of Ti Colloid
$TiCl_4$ was mixed with ethanol : H_2O in the specified composition in the flask and added NH_4OH up to pH about 7. The mixture was stirred to obtain white mixture.

Preparation of magnetite colloid
$FeCl_3$, $FeCl_2$ and NH_4OH were mixed and placed on the flask. The N_2 gas was flowed into the mixture for a specified periods and then the solid was filtered and added by TMAOH in the presence of stirrer

Preparation of bentonite suspension
Ti, Fe colloid and bentonite suspension were mixed in the reflux flask. The mixture was stirred and heated up to keep temperature about 50 ° C for spesified periods. Then the mixture was filtered, washed with ethanol : H_2O mixture and dried in the oven. Dried material was size reduced up to 140 mesh.

Calcination procedure
A spesified mass of photocatalyst was fed into the calcination tube and heated up in the calcination furnace. The condition was set up at specified calcination temperature and time. N_2 and O_2 gas was flowed alternately for specified rate.

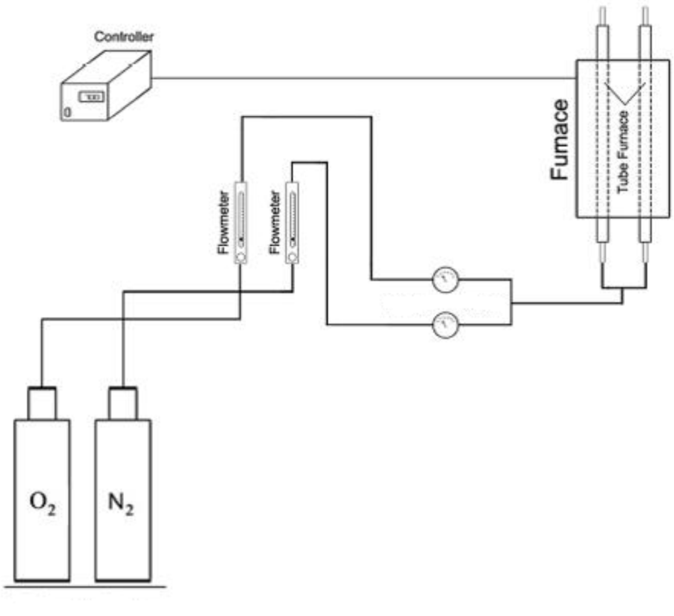

Figure 1. The Calcination Equipment

Photocatalyst material characterization
The material was analyzed by XRD (X-Ray Diffraction) for each photocatalysts have been made. The characterization was aimed to determine whether the Fe and Ti affect bentonite structure.

Photocatalytic activity test material against degradation of phenol

The specified mass of photocatalyst material was added to the phenol solution with a certain concentration. The solution was exposed under UV light and sunlight for certain periods. After process, the solid was filtered and the filtrate was adjusted to the pH 7.9 ± 0.1 with the addition of phosphate buffer solution. It was also added by aminoantipirin and potassium ferisianida. The samples were analyzed by spektrofotometer at 510 nm wavelength.

RESULTS AND DISCUSSION

The characterization of TiO_2/Fe_3O_4-Bentonite was conducted by X-Rays Diffraction. The analysis was conducted to observe the influence of the calcination temperature on the anatase phase (TiO_2) and magnetite phase (Fe_3O_4) on the bentonite as support.

The effect of calcination temperature on the anatase phase (TiO_2) and magnetite phase (Fe_3O_4) on bentonite as support

Generally, anatase phase appears to be more dominant on the temperature calcination 500 ºC to 600 ºC and otherwise, at 700 ° C the rutile phase of TiO_2 appear to be more dominant because high temperature changes the crystal phase (anatase phase into rutile phase).

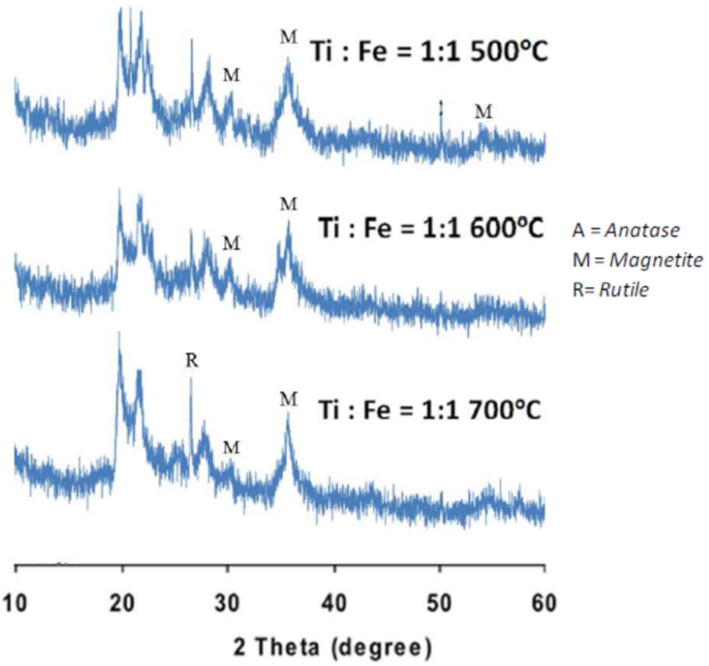

Figure 2. The XRD analysis at ration Ti : Fe = 1 : 1 at various calcination temperature

Table 1. The Intensity of Diffraction Peak of Photocatalyst at ratio Ti : Fe = 1 : 1

2θ	Intensity of Diffraction Peak (%)						
	500 ºC		600 ºC		700 ºC		
	Anatase	Magnetite	Anatase	Magnetite	Anatase	Magnetite	Rutile
27.446 (R)							33.05
30.105 (M)		26.35		28.45		12.67	
35.451 (M)		47.44		68.14		58.72	
53.478 (M)		11.83					

The Figure 2 and Table 1 showed the XRD analysis of photocatalyst material at ratio of Ti: Fe = 1: 1 The dominant phase of material was magnetite. It is caused the calcination process tend to form iron oxide and titanium oxide. The iron oxide was more easily to react rather than titanium dioxide. Moreover, it might be the anatase phase that was formed on calcination temperatures at 500 and 600 ºC was amorphous region. It was difficult to detect the amorphous phase on the XRD analysis. But at the calcination temperature at 700 ºC rutile phase began to form.

At high temperature, the stability of rutile structure is higher than anatase phase. The O atoms tended to bond to Ti creating the rutile phase. This is consistent with the theory that state high temperature might change the crystalline phase of TiO_2 from anatase phase into rutile phase. From the table 1, it can be seen that for the ratio of Ti: Fe = 1: 1 and calcination temperature of 600 ºC, the intensity of the diffraction peak reached 68.14 % for magnetite phase. This was the greatest intensity of magnetite phase rather than other.

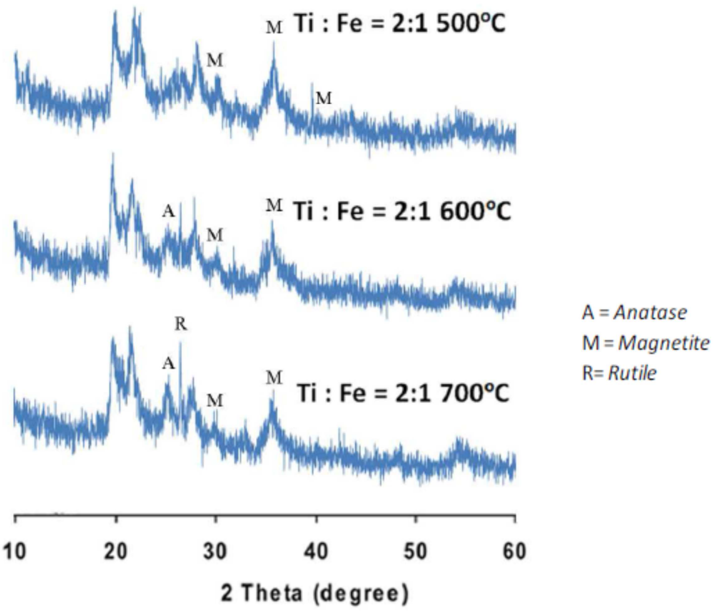

Figure 3. The XRD analysis at ratio Ti : Fe = 2 : 1 at various calcination temperature

Table 2. The Intensity of Diffraction Peak of Photocatalyst at ratio Ti : Fe = 2 : 1

2θ	Intensity of Diffraction Peak (%)						
	500 ºC		600 ºC		700 ºC		
	Anatase	Magnetite	Anatase	Magnetite	Anatase	Magnetite	Rutile
25.281 (A)			27.46		42.08		
27.446 (R)							40.84
30.105 (M)		25.29		13.95		11.75	
35.451 (M)		72.51		52.88		38.87	
43.123 (M)		9.52					

Figure 3 showed that for ratio Ti: Fe = 2: 1 anatase phase was appeared, especially at high calcination temperature (600 ºC and 700 ºC). The higher the amount of Ti on the composite , the higher the intensity of the anatase phase. At high temperature (700 ° C), rutile phase appeared at the XRD spectra. In this temperature, the phase of crystal was dominated by rutile phase. Otherwise, the magnetite phase of Fe_3O_4 still persists, although the amount of Fe in the composite was reduced. It is caused that the oxidation of Fe is easily occured rathe than the oxidation of Ti. The results showed that at ratio of Ti : Fe = 2: 1 and the calcination temperature 600 ºC gave relatively better material on the aspect of anastase region rathe than other temperature. At 600 ºC, the photocatalyst was dominated by anatase and magnetite phase. Both of them were responsible for decomposing the phenolic compound. However, for the ratio of Ti: Fe = 2 : 1 at the calcination temperature 700 ° C, the rutile phase also appeared on the material. Increasing rutile phase on the crystal will reduce the number of anastase phase. It affected on the activity of photocatalysis. The activity photocatalyst will be lower.

Figure 4 and Table 3 showed that the dominant phase on the photocatalyst material was rutile and magnetite phase. At this condition the magnetite phase had the highest value on magnetite phase. It might be caused the amount of Fe was the highest compared other ratio.

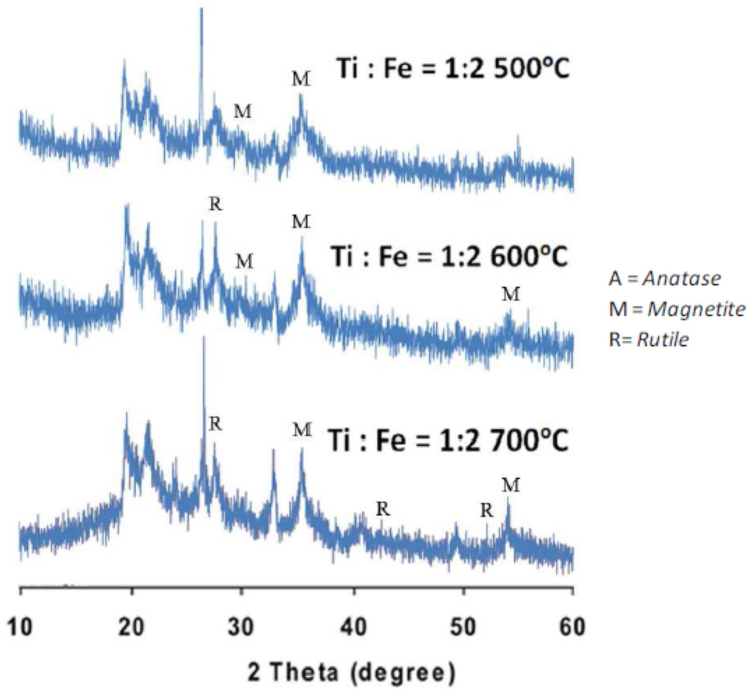

Figure 4. The XRD analysis at ratio Ti : Fe = 1 : 2 at various calcination temperature

Beside magnetite phase, the rutile phase was also dominant at the calcination temperature 600 and 700 ºC. It is due to the stability of rutile structure was high at higher temperature.

The atoms O were bonded to Ti to form titanium dioxide in the form of rutile phase. Acording to Figure 4 and Table 3, it can stated that the ratio of Ti : Fe = 1 : 2 at calcination temperature 600 ºC gave relatively better material than it on other condition. The percentage of magnetite phase of material at the calcination temperature of 600 ºC was 60.55%.

2θ	Intensity of Diffraction Peak (%)							
	500 ºC		600 ºC			700 ºC		
	Anatase	Magnetite	Anatase	Magnetite	Rutile	Anatase	Magnetite	Rutile
27.446 (R)					51.97			31.52
30.105 (M)		3.21		14.94				
35.451 (M)		12.66		60.55			35.67	
41 (R)								10.19
43.123 (M)				17.32				20.06

The Performance of Photocatalyst Materials on Degradation Phenolic Compound
The analysis of the relation between the characterization of material and the photocatalyst ability of Ti / Fe-bentonite composite has been already conducted as shown on Table 4.

Table 4 The Performance of Photocatalyst Material on Degradation Phenolic Compound

Ratio	0 min	30 min		60 min	
Ti : Fe	C, ppm	C, ppm	% conversion	C, ppm	% conversion
1 : 2	299.462	285.231	4.752	253.308	15.412
2 : 1	282.154	259.846	7.906	236.769	16.085
1 : 1	312.538	291	6.891	267.154	14.521

Based on the data it can be seen that the longer the UV exposure time, the conversion of phenol increased. The higher conversion occured when the degradation process used the photocatalyst at 600 ºC and ratio of Ti: Fe = 2 : 1. This is in line with the characterization results using X-ray diffraction, where the ratio of Ti : Fe = 2 : 1 gave the anatase and magnetite phase. Anatase and magnetite phase play a role to decompose the phenolic compound. Anatase phase is the main phase to decompose the phenolic compound. The photocatalytic activity of the anatase phase is higher than that of the magnetite phase. While the ratio of Ti : Fe = 1: 2 and Ti : Fe = 1 : 1, the dominant phase was only magnetitenya phase and anatase phase is not formed, it affected on lowering decomposition ability of photocatalyst material.

CONCLUSION

The conclusions of the research were
1. The ratio of Ti:Fe 1:1 and 1:2 gave photocatalyst material which have magnetite phase more dominant than other phase, Otherwise anatase phase was formed on higher ration of Ti : Fe (2:1)
2. At 500 ºC, photocatalyst had magnetite phase as dominant phase. At 600 ºC, the dominant phase was anatase and magnetite, other wise at 700 ºC, magnetite and rutile phase were created. On this study, 600 º C of calcication temperature gave better material than other condition
3. The higher conversion was conducted on Ti:Fe 2 :1 at 600 ºC calcination Temperature for 60 min UV exposed. The conversion of phenol reached as 16.085 %

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