PREPARATION OF TiO_2-Fe_3O_4 SUPPORTED BENTONITE AND ITS ACTIVITY TEST FOR PHOTOCATALYTIC DEGRADATION OF PHENOL

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Abstract

The bentonite suspension was prepared and used as porous support for synthesis of TiO_2-Fe_3O_4 based photocatalyst with varying TiO_2 loading. The variations TiO_2-Fe_3O_4 of in this experiment were 1:1 and 2:1. the synthesis of the photocatalytic materials have been carried out by sol-gel method and followed by calcination. The temperatures of calciantion were varried at 500, 600 and 700°C. The physicochemical properties of TiO_2-Fe_3O_4 bentonite samples were characterised by X-ray diffraction. Photocatalytic activity of the materials was evaluated by phenol photodegradation using 20W UV light for 60 minutes. The titania content in the materials significantly influenced the physicochemical properties and catalytic activity.

Keywords:TiO_2, anatase, bentonite, photocatalytic, phenol degradation

I. Introduction

Photodegradation of pollutants using semiconductor photocatalys with solar light can make it an economically viable process since solar energi is an abundant and inexpensive natural energi source [1]. Titania oxide (TiO_2) is an example the semiconductor materials with wide band gap energy and nontoxicity. This materials is widely used as gas sensors [2], pigment [3], solar-energy conversion [4] and a promising photocatalyst for water and air purification [5–9], dyes adsorption [10] and degradation [11] because of its high oxidative power, chemical stability, low cost, and nontoxicity [12]. Unfortunately, one severe disadvantage of the TiO_2 semiconductor material is the large band gap of 3.0 or 3.2 eV in the rutile or anatase crystalline phase, respectively and only absorbs the UV light which accounts for merely 5% of the solar spectrum. Therefore, there have been many efforts to extend activity of TiO_2 into the visible region to improve utilize efficiency of TiO_2 [13–15]. In addition, the use of titania in bulk form suffers from catalyst recovery and activity reduction, which results in ineffective application of the catalyst. In some cases, fine titania particles could also block the penetration of light into the solution. To overcome the limitations, several approaches were proposed e.g. attaching titania particles onto stable inorganic supports [16-19]. In principle, inorganic materials with high specific surface area and chemical stability can be used as host matrix. Natural porous materials such as zeolites and clay minerals are also good and cheaper supports with eco-friendly properties. Some research that synthesize of iron oxide as photocatalyst materials have been done. Karna etc., 2005, synthesize of Fe_2O_3 on montmorilonite as supporting materials and used it as photocatalyst on photodegradation of congo red

dye. The preparation of iron oxide on the structure of natural montmorillonite are the specific surface area of the montmorillonite also increased significantly from $9,71 m^2/g$ to $126,49\ m^2/g$ and total pores volume increased from 50.70×10^{-3} mL/Å/g to 107.89×10 mL/Å/g, respectively. Photodegradation of congo red using Fe_2O_3-montmorillonite caused the decreament of congo red concentration up to 90.22 % on UV illumination for 60 minutes. Adsorption of congo red on Fe_2O_3-montmorillonite reached 84.4% and on montmorillonite Was 75.15%.

Bentonite, one kind of clay minerals, possess high porosity, exchangeable cations and swellable properties. Previously, several researchers reported the preparation of titania immobilization on clay minerals via pillarization processes. However, during the preparation, highly acidic environment of titanium pillaring precursor damages the structure of clay minerals [20,21]. Accordingly, the low crystallinity of supported titania would have a reduced capability of catalyst in catalysis. Additionally, the preparation showed not very good reproducibility [22]. Recently, some investigations reported that the used of several metals, such as Al, Zr and Fe as pillaring precursors for preparation of pillared clay minerals for synthesis of supported TiO_2 or TiO_2 composites as catalysts, showed the catalysts have higher thermal stability and specific surface area [23-27].

This paper deals with the phenol degradation on the catalyst activity of TiO_2-Fe_3O_4 immobilized in bentonite. This paper also deals with the ratio of TiO_2-Fe_3O_4 loading.

II.   Experimental

The starting clay was a natural Pacitan bentonite, extracted from Pacitan region, East Java, Indonesia. The preparation of TiO_2-Fe_3O_4 based photocatalyst was based on modification of Massart method by sol-gel method. The material was prepared by mixing colloidal Ti (from $TiCl_4$, Merck) and colloidal Fe (from $FeCl_2$ and $FeCl_3$, Merck) which has mol ratio of 1:1 and 2:1, and the ammount of Fe is 25 mol. Immobilization process was carried out by mixing this colloid with bentonite suspension. The mixture was heated at 50^oC. After 24 hours, the mixture was cooled and washed with aquadest. The obtained solid was dried and calcined at 700^oC for 4 hours with nitrogen and oxygen stream. All the materials were systematically characterized by powder X-ray diffraction (Shimadzu XRD 1000).

The catalytic performance of catalyst materials was carried out in a batch glass reactor equipped with thermometerfor photocatalytic degradation of phenol. It was open to the atmosphere and thoroughly stirring with magnetic stirrer. The reaction was conducted at 30^oC for 60 minutes. The initial molar ratio of phenol was 400 ppm; the weight of catalyst was 0.25 g. The course of the phenol degradation was followed by uv-vis spectrophotometer means of Genesis 10. Conversion is defined as the ratio of consumed phenol over the fed phenol for the reaction.

III.   Result and Discussion

The XRD patterns of natural bentonite showed the characteristic peaks at $2\theta=6.3°$ ($d001=14.9$ Å) as main peak and $2\theta=19.9°$ ($d=4.5$ Å). Other reflections at $21.8°$ and $26.6°$ indicated crystoballite and quartz (Fig. 1). Reflections of titania on Nat. Bent-Ti:Fe (1:1 and 2:1) were observed. The titania phase was identified at 2θ $25.1°$, $37.7°$, and $61.8°$ at the XRD pattern of standar anatase phase. These reflections indicated tetragonal titania (anatase). In addition, the magnetite phase was identified at 2θ $35.6°$ and $30.3°$ at the XRD pattern of standart magnetite phase.
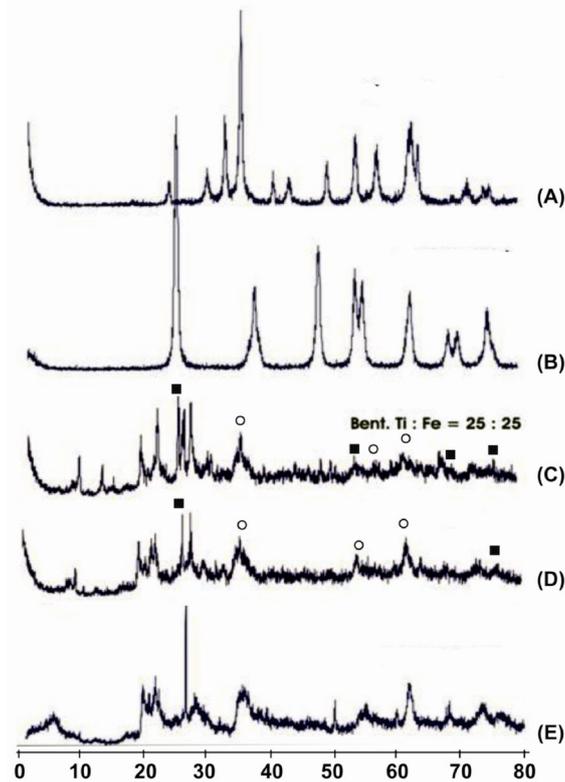
Fig 1. XRD difractogram of bentonite TiO$_2$-Fe$_3$O$_4$ in ratio molar variation. (A) Magnetite (Fe3O4); (B) Anatase (TiO2); (C) Natural Bentonite- (Ti : Fe = 25 : 25) mmol; (D) Natural Bentonite-(Ti : Fe = 50 : 25) mmol; (E) Fresh Bentonite. ■ = Anatase; ○ = Magnetite

The XRD pattern showed that the intensity main peak of the anatase phase showed at $2\theta = 25.28$ higher than magnetite phase at $2\theta = 35.45$. The basal peak of natural bentonite showed at $2\theta = 5.8$ before metal doped and calcinatiaon at 500 ^{o}C . After that, the main peak of natural bentonite basal peak increase to $2\theta = 9.98$. This phenomena may effect by iron oxide and titanium oxide that make collapse the bentonite structure. The basal peak of anatase at bentonite (Ti:Fe) = 1:1 higher than bentonite (Ti:Fe) = 2:1. This indicate that the crystallinity of anatase at bentonite (Ti:Fe) = 1:1 better than bentonite (Ti:Fe) = 2:1. The main basal of magnetite at bentonite (Ti:Fe) = 2:1 higher than bentonite (Ti:Fe) = 1:1, we conclude that the crystallinity of magnetite at Ti:Fe = 2:1 ratio, better than Ti:Fe = 1:1 ratio and more dominat than anatase phase.

Tabel 1. The effect of tiatanium and iron content to surface area and pore volume of bentonite..

No.	Nama Katalis	Jml. Logam (% massa)		Luas permukaan katalis (m^2/g)	Volume total (ml/g)
		Ti	Fe		
1.	Fresh Bentonit	0	0	34.17	0.14
3.	Bent. – Ti : Fe = 25 : 25	1.94	3.31	144.4	0.176
4.	Bent. – Ti : Fe = 50 : 25	13.12	6.9	109.6	0.185

The effect of titanium and iron content to bentonite structure is changed the surface area and pore volume of bentonite (Table.1). The spsesific surface area of bentonite

(Ti:Fe) = (25:25) mmol is 144.4 m^2/g higher than bentonite (Ti:Fe) = 2:1 109.6 m^2/g and fresh bentonte 34.17 m^2/g but pore volume bentonite (Ti:Fe) = 2:1 is 0.185 ml/g higher than bentonite (Ti:Fe) = 1:1 is 0.176 ml/g and 0.14 ml/g.

The photocatalytic activity of various catalysts in phenol photodegradation is presented in table 1. The result show that no reaction in absence of catalyst. Fresh bentonite showed the lowest degradation activity. The reducing of phenol in reaction using fresh bentonite as a result of adsorption process of phenol at the bentonite surface. The other materials exhibited varying activity depending on Ti loading and material phase. The catalytic activity followed the order magnetite > anatase > Bent Ti:Fe 1:2 > Bent Ti:Fe 2:1. This data showed very clearly that anatase and magnetite was responsible material for phenol photodegradation. When Ti and Fe was supported in bentonite, then the catalytic activity was lower than that of anatse and magnetite. This is probably due to the textural change and surface distribution of TiO_2 and Fe_3O_4. Loading TiO_2 and Fe_3O_4 might be reduce the specific surface area, which brought about low adsorption of phenol on catalyst surface for the phenol to be contacted with TiO_2 and/or Fe_3O_4 for photo reaction. In addition, this is also probably because of aggregation of TiO_2 and/or Fe_3O_4. it cause reducing TiO_2 and/or Fe_3O_4 on bentonite making less amount of active sites than those of anatase and magnetite.

Table 1. photocatalyric performance of bentonite TiO_2-Fe_3O_4

Catalyst	Phenol conversion (%)
Without catalyst	-
Fresh bentonite	10
Anatase	48
Magnetite	52
Bent Ti:Fe (25:25) mmol	18
Bent Ti:Fe (50:25) mmol	14

4. Conclusion

The result showed that the crystallinity of anatase phase higher than magnetite at the Ti:Fe ratio is (25:25) mmol and the crystallinity of magnetite better than anatase at the Ti:Fe ratio is (50:25) mmol. The Ti-Fe content on the bentonite structure are succesfully increase surface area and pore volume of bentonite. The Ti:Fe ratio is (25:25) mmol increase the spesific surface area is 144.4 m^2/g, higher than Ti:Fe ratio is (50:25) mmol and pore volume of Ti:Fe ratio is (50:25) mmol is 0.185 ml/g higher than Ti:Fe ratio is (25:25) mmol.

However, the photocatalytic activity of bent-Ti:Fe for phenol degradation was not very high. The synthesis of catalyst materials still need to be improved.

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Refference

[1] Wang, X., Meng, S., Zhang, X., Wang, H., Zhong, W., Du, Q., Chem. Phys. Lett. 444 (2007) 292

[2] V. Guidi, M.C. Carrota, M. Ferroni, G. Martinelli, Sensor Actuat. B: Chem. 57 (1999) 197.

[3] C. Feldmann, Adv. Mater. 13 (2001) 1301.

[4] P.V. Kamat, N.M. Dimitrijevic, Sol. Energy 44 (1990) 83.

[5] M. Gratzel, Nature 414 (2001) 338.

[6] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

[7] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.

[8] Fujishima, A., Zhang, X., Tryk, D.A., Int. J. Hyd. Ene. 32 (2007) 2664

[9] Rajeshwar, K., Osugi, M.E., Chanmanee, W., Chenthamarakshan, C.R., Zanoni, Kajitvichyanukul, P., Krishnan-Ayera, R., J. Photochem. Photobiol. C. 9 (2008) 15

[10] Koswojo, R., Utomo, R.P., Ju, Y.H., Ayucitra, A., Soetaredjo, F.E., Sunarso, J., Ismadji, S., Appl. Clay Sci. 48 (2010) 81

[11] Is Fatimah, I., Wang, S., Narsito, Wijaya, K., Appl. Clay Sci. 50 (2010) 588

[12] A.L. Linsebigler, G.Q. Lu, T. Yates, Chem. Rev. 95 (1995) 735.

[13] C. Xu, R. Killmeyer, M. Gray, S.U.M. Khan, Appl. Catal. B: Environ. 64 (2006) 312.

[14] R.Y. Hong, J.Z. Qian, J.X. Cao, Powder Technol. 163 (2006) 160.

[15] Y.Z. Li, D. Hwang, N.H. Lee, S. Kim, Chem. Phys. Lett. 404 (2005) 25.

[16] Mahmoudi, N.M., Arami, M., J. Photochem. Photobiol. B. 94 (2009) 20.

[17] Reddy, E.P., Davydov, L., Smirniotis, P., Appl. Catal. B 42 (2003) 1.

[18] Li, F., Sun, S., Jiang, Y., Xia, M., Sun, M., Xue, B., J. Haz. Mat. 152 (2008) 1037

[19] Shieh, J.K, Min Li, Lee, Y.H., Sheu, S., Liu, Y., Wang, Y.C., Nanomed.: Nanotech. Biol. Med. 2 (2006) 121

[20] Bergaya, F., Theng, B.K.G., Lagaly, G., Handbook of Clay Science, Developments in Clay Science, Vol. 1 (2006), Elsevier Science, Amsterdam.

[21] Yuan, Peng, Yin, Xiaolin He, Hongping, Yang, Dan, Wang, Zhu, Linjiang, Jianxi, Micro. Meso. Mat. 93 (2006) 240.

[22] Romero, A., Dorado, F., Asencio, I., Garcia, P.B., Valverde, L., Clays Clay Miner. 54 (2006) 737

[23] An, T.C., Chen, J.X., Li, G.Y., Ding, X.J., Sheng, G.Y., Fu, J.M., Mai, B.X., O'Shea, K.E., Catal. Today 139 (2008) 69

[24] Belessi, V., Lambropoulou, D., Konstantinou, I., Katsoulidis, A., Pomonis, P., Petridis, D., Albanis, T., Appl. Catal. B 73 (2007) 292

[25] Daniel, L.M., Frost, R.L., Zhu, H.Y., J. Col. Inter. Sci. 316 (2007) 72.

[26] Daniel, L.M., Frost, R.L., Zhu, H.Y., J. Col. Inter. Sci. 322 (2008) 190

[27] Menesi, J., Korosi, L., Bazso, E., Zollmer, V., Richardt, A., Dekany, I., Chemosphere 70 (2008) 538