STUDY OF PHOTOCATALYTIC DEGRADATION OF BASIC BLUE ON TiO_2-Fe_3O_4 PILLARED BENTONITE

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ABSTRACT

was prepared and used as porous support for synthesis of TiO_2-Fe_3O_4 based photocatalyst with varying TiO_2 and Fe_3O_4 loading supported by surfactant molecule pillared bentonite has been carried out. The raw bentonite was obtained from Pacitan, Indonesia. The surfactant molecule was Tetra Methyl Ammonium salt. The variations of TiO_2-Fe_3O_4 in this experiment were 1:3 and 3:1. Synthesis of the photocatalytic materials have been done by sol-gel method and followed by calcinations at 500°C. In order to characterize the structure of photocatalytic material that has been synthesized, X-ray diffraction method was performed. Photocatalytic activity of the materials was evaluated by basic blue photo degradation using UV light.

The titania and magnetite content in the materials significantly influenced the physicochemical properties and catalytic activity.

Keywords:TiO_2, Fe_3O_4, bentonite, photocatalytic, basic blue degradation

INTRODUCTION

As we stepped into this century, we are facing the challenge of purification of water resources. One of the water pollutants is dyes. In spite of many uses, the dyes are toxic and carcinogenic in nature and environmental contamination by these toxic chemicals is emerging as a serious global problem. Coloured solution containing dyes from industrial effluents of textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage. On the other hand, bleached dye solution is less toxic and almost harmless. Secondly, dye containing coloured water is of almost no use, but if this coloured solution is bleached to give colourless water, then it may be used for washing, cooling, irrigation and cleaning purpose. The photocatalytic bleaching seems to be quite promising and can provide a low cost method to solve this problem. The uses of TiO_2 as photocatalyst have been excellently reported by some researchers [1-8]. However, 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. by optimizing the nanostructure of TiO_2, using various processing routes, such as a sol-gel method [9], by doping with a transition metal oxide such as F_3O_4 [10], attaching titania particles onto stable inorganic supports [10,11]. 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.

Bentonite as a clay minerals own high porosity, exchangeable cations and swellable properties. Previously, some researchers reported that during the preparation of titania immobilization on clay minerals via pillarization processes, titania was incorporated in the interlayer space of the clay through an intercalation step of pillaring precursors via ionic species. Recently, some investigations reported the synthesis of supported TiO_2 or TiO_2 composites as catalysts [2, 12-17].

In this paper, we report preparation of pillared Indonesian Bentonite and its use as a support for Fe_3O_4-doped TiO_2 immobilization. These photocatalyst were characterized by X Ray Diffraction and tested for photodegradation of basic blue.

EXPERIMENTAL SECTION

The starting clay was a natural Pacitan bentonite, extracted from Pacitan region, East Java, Indonesia. Initially, as-collected bentonite was dried in forced-circulation oven at 110 °C to remove excess moisture content. The drying process was carried out for 24 h. Subsequently, dried bentonite was crushed to obtain powder bentonite with a particle size of 60/80 mesh. 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 molar ratio of 1:3 and 3:1. Immobilization process was carried out by mixing this colloid with bentonite suspension. The mixture was heated at 50^{o}C. After 24 hours, the mixture was cooled and washed with aquadest. The obtained solid was dried and calcined at 500^{o}C 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 thermometer for photocatalytic degradation of basic blue. It was open to the atmosphere and thoroughly stirring with magnetic stirrer. The reaction was conducted at 30^{o}C for 120 minutes. The initial molar ratio of basic blue was 300 ppm; the weight of catalyst was 0.25 g. Irradiation was carried out by keeping the whole assembly exposed to a 100 W mercury lamp. The course of the basic blue degradation was followed by uv-vis spectrophotometer means of Genesis 10. Conversion is defined as the ratio of consumed basic blue over the fed basic blue for the reaction.

RESULTS AND DISCUSSION

Catalyst Characterization

We reported the XRD patterns of bentonite (montmorillonite) in our previous study [2]. It showed the characteristic reflections at $2\theta=6.3°$ ($d001=14.9$ Å) and $2\theta=19.9°$ ($d=4.5$ Å). Other reflections at 21.8° and 26.6° indicated crystoballite and quartz. Figure 1 depicts reflections of titania on Bent-Ti:Fe (1:3 and 3:1). The titania phase was identified at 2θ 25.1°, 37.7°, and 61.8°. These reflections indicated tetragonal titania (anatase). In addition, the magnetite phase was identified at 2θ 35.6° and 30.3°. However, the intensity of the anatase and magnetite phase was low. Additionally, the (101) reflection of rutile at 27° was found. Titania crystallization at high loading was also observed in the preparation of nanoparticle titania membranes and titania incorporation in gels reported in previous studies, where both anatase and rutile forms were produced. In the pillared bentonite anatase was generally formed or sometimes no reflections of titania were found [17-20]. The hydrolysis rate of $TiCl_4$ may affect the titania and crystallization in the bentonite. Titanium and Fe would be fast deposited in gel form before it reached the bentonite pores [17]. Due to the gel form with larger molecular size, $TiCl_4$ were difficult to penetrate into the pores of bentonite and the condition would favor the formation of both anatase and rutile during the crystallization process. Figure 1 also shows that intensity of tetragonal titania (anatase) in Bent-Ti:Fe (3:1) is higher than the intensity of magnetite compare to that of in Bent- Ti:Fe (1:3). This is due to higher loading of titania in Bent-Ti:Fe (3:1).

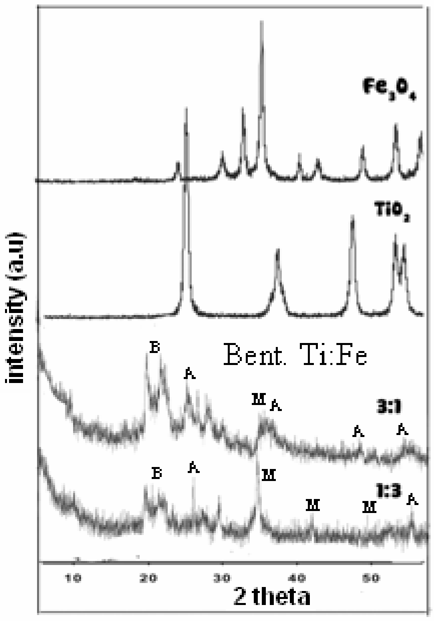

Fig 1. XRD difractogram of bentonite TiO_2-Fe_3O_4 in ratio molar variation

Photodegradation of Basic Blue

The photocatalytic degradation of basic blue was observed at λmax = 600 nm. The results of a typical run are graphically represented in Fig. 2.

In Fig.2 it was observed that with an increase in titania loading in the catalyst material, the capability of photocatalytic degradation of the dye decreases. This behavior can be explained on the basis that as the titania loading increases, more rutile phase are available rather than that of anatase phase (Fig. 1). This is probably due to the textural change and surface distribution of TiO_2. Loading of TiO_2 reduced the specific surface area, which resulted in low adsorption of basic blue on catalyst surface for the basic blue to be contacted with TiO_2 anatase for reaction. In addition, the aggregation of TiO_2 in

Bent-Ti-Fe (3:1) might also reduce its dispersion on bentonite, making fewer amounts of active sites than those on Bent-Ti-Fe (1:3) and thus a lower activity of Bent-Ti-Fe (3:1). Due to the anatase phase are considered responsible for the photocatalytic bleaching of basic blue, the decreasing of anatase phase causes decreasing of the activity of photocatalytic degradation of the dye. The absence of bentonite in the catalyst material causes the decreasing of the photodegradation activity. By attaching titania particles onto stable inorganic supports (bentonite), the crystallinity of titania might be enhance. Fig.2. also depicts that photodegradation time of basic blue on these catalyst materials is optimum in 20 minutes.

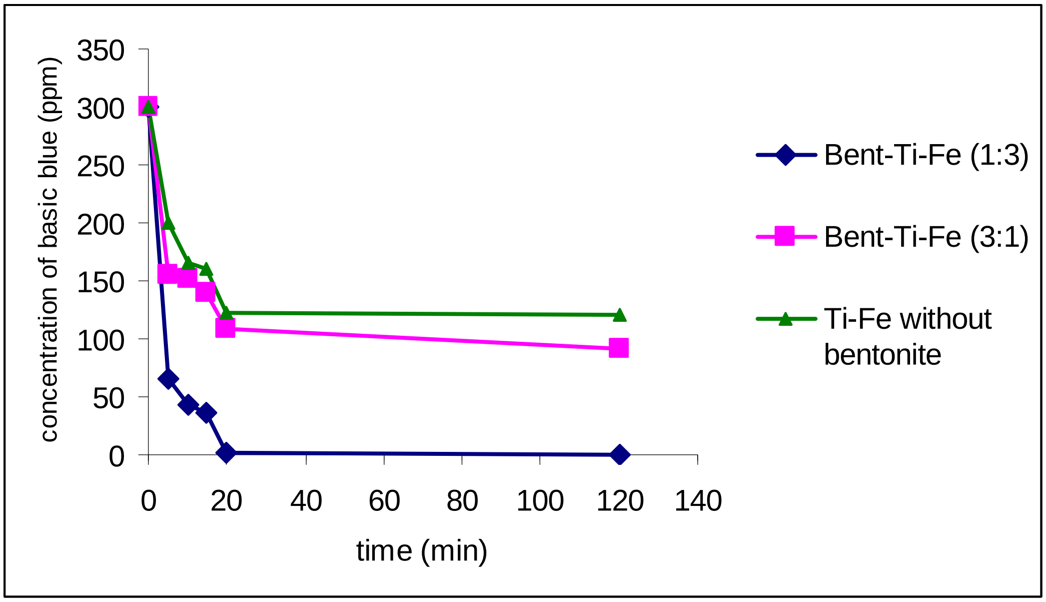

Fig.2. Effect of titania loading in catalyst on the activity of photocatalytic degradation of basic blue

CONCLUSION

The photocatalytic decolourization of basic blue over TiO_2-Fe_3O_4 pillared bentonite provides an ecofriendly method for degradation of the dye. The titania and magnetite content in the materials significantly influenced the physicochemical properties and catalytic activity.

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