IOP Conference Series: Materials Science and Engineering

The effect of Titanium dioxide precursors variation to morphology of TiO_2/ZSM-5 composite

The effect of Titanium dioxide precursors variation to morphology of TiO_2/ ZSM-5 composite

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Abstract. TiO_2 photocatalyst is one of the Advanced Oxidation Processes (AOPs) methods which is very potential to be applied to treat wastewater. Modification of TiO_2 with the addition of ZSM-5 as supporting material can increase the adsorption capacity and conductivity of water molecules. Those properties enable TiO_2/ ZSM5 composites to conduct photodegradation process within dye waste. TiO_2/ ZSM5 composites were prepared by sol gel method. The synthesized materials were characterized by X-ray diffraction (XRD), Energy Dispersive X-ray Scanning Electron Microscopy (SEM-EDX), and Brunauer-Emmett-Teller (BET). The effect of 2-Propanol to TiO_2/ZSM-5 Composite Morphology was studied. The results from X-Ray Diffraction analysis revealed that the peak indicating the presence of anatase TiO_2 on sample 2.5;5; and 10% TiO_2/ZSM-5 composite. The increasing effect of Titanium precursors to TiO_2/ ZSM-5 composite carried out agglomerates on external surface of ZSM-5 as seen in SEM which was supported by surface area data from BET.
Keyword : Photocatalyst, Sol- gel, TiO_2, ZSM-5

1. Introduction

At present, the development of Indonesia's textile industries is growing rapidly. The use of dyes in the textile industry causes problems, namely, waste produced is still coloured and difficult to degrade [1]. Dyes waste contains aromatic complex compounds which are difficult to decompose by microorganisms [2]. Due to these problems, it becomes very important to process dyes waste before it discharges into the water bodies. This treatment process is expected to reduce the negative impacts of dye waste.

Several methods have been developed to process and reduce dye waste. Those methods are adsorption, coagulation, and membrane filtration. However, adsorption and coagulation methods produce several secondary contaminants that require further processing, while the membrane filtration method is very expensive [3]. Currently, a new method is being developed to treat dyes waste, namely the AOPs method. This method employs several processes which involve hydrogen peroxide (H_2O_2), UV light, photocatalyst titanium dioxide, and several other processes to produce hydroxyl radical. This method produces far fever residues compared to conventional methods [4]. Due to this property, the AOPs method has attracted the attention of many researchers. The photocatalyst method using a TiO_2 semiconductor illuminated with UV light or visible light is one of the AOPs methods which is very

IOP Conf. Series: Materials Science and Engineering **588** (2019) 012037 doi:10.1088/1757-899X/588/1/012037

potential to be applied to treat wastewater [5]. It is known that TiO_2 has high chemical stability, cheap, non-toxic and sufficient availability. The presence of those properties makes TiO_2 a very suitable material for the AOPs method. However, it is figured out that TiO_2 still has a deficiency, the band gap of TiO_2 is quite wide (3.2 eV). The wide band gap makes TiO_2 only active in the UV light region, thus limiting its usage and efficiency in its application process [6]. To overcome these shortcomings, such as hexagonal mesoporous silica (HMS) or zeolite are applied as additional porous support materials on TiO_2 [7] [8].

Zeolites as porous materials can increase surface area, hydrophilic or hydrophobic properties and expected to improve adsorption capacity and facilitating the process of substance diffusion [9]. One of materials which can be applied for high specification TiO_2 modification is ZSM-5. ZSM-5 has a pore size (5.3 Å), particle size, and it is easily synthesized according to research which has been conducted by Hartanto [10][11][12].

Modification of TiO_2 with the addition of ZSM-5 as supporting material can increase the adsorption capacity and conductivity of water molecules so that TiO_2/ZSM-5 composites possess high hydrophilic properties [13]. Those properties enable TiO_2/ZSM5 composites to conduct the photodegradation process within dye waste [14] [15].

When TiO_2 with particle size 30 Å is added to ZSM-5 with pore size 5.3 Å, TiO_2 will not be dispersed equivalently over the pores and will only affect the external surface, pore volume and mesopore volume becomes bigger [16][17]. This study focused on morphology and external surface area of TiO_2/ ZSM-5 composite materials after the addition of the various 2-Propanol.

2. Experimental

2.1. Materials

The materials used were commercial ZSM-5 with Si/Al = 50 from Acros Organic, titanium(IV) isopropoxide (TiIP) (97%, Aldrich), titanium dioxide (TiO_2) (98%, Acros Organic), aluminum oxide (Sigma-Aldrich), and 2-propanol (97%, Merck).

2.2. Methods

Synthesis TiO_2/ZSM-5 was carried out using sol-gel method. TiO_2 precursors, which is Titanium isopropoxide (TiIP) and 2-propanol was mixed under constant stirring for 5 minutes. Then ZSM-5 powder was added into the resulting solution. The amount of ZSM-5 was fixed while the amount of TiO_2 precursors was varied to analyze it's effect to composite morphology. Variation of TiO_2 precursors used is 2.5; 5; and 10 percent weight of ZSM-5.

Then the mixture of TiO_2 precursors and ZSM-5 was stirred for another minutes until a gel formed. The gel then dried for 12 hours in oven to form a white powder that further being calcined in 550 °C furnace for 3 hours. The resulting powder then characterized using XRD to identify phase and cristallinity of the resulting composite. SEM measurements was carried out to analyse morphological structure.

3. Result and Discussion

3.1. X-Ray Diffraction (XRD) Analysis

X-Ray Diffraction analysis was carried out to characterize the crystal structure of the material. Sample TiO_2/ZSM-5 composite with the variation of TiO_2 2.5; 5; and 10% weight was characterized by XRD, as shown in Figure 1.

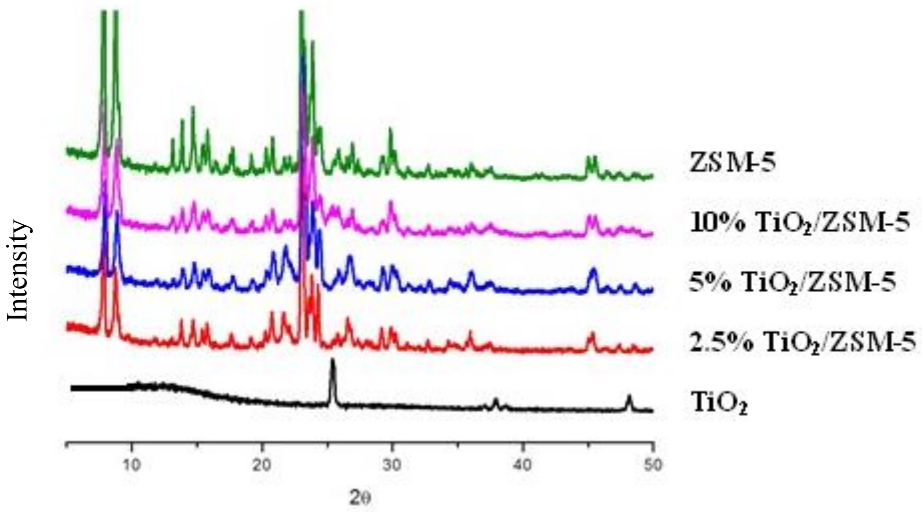

Figure 1. XRD patterns of TiO_2/ZSM-5 composite with variation of TiO_2 percent weight

From this diffractogram, all composite samples are indicating the presence of MFI structure (2θ =7-10° and 22-35°) and the anatase phase of TiO_2 (2θ = 25.3°). The peak of anatase TiO_2 on sample 2.5;5; and 10% TiO_2/ZSM-5 composite is broader than the peak of TiO_2 pure because this peak merged with ZSM-5's peak around 25°. The addition of TiO_2 does not affect the crystal structure of ZSM-5. It caused by ZSM-5 suppresses the growth of TiO_2 during the synthesis process [8]

3.2. Scanning Electron Microscope – Electron Dispersion X Ray (SEM-EDX)

SEM-EDX is used to analyze the morphology and distribution of elements in a material. Commercial ZSM-5 was characterized by SEM, as shown in figure 2a. From this image, ZSM-5 has a hexagonal shape that indicates the sample has a high crystallinity [18]. Some sphere like shape around the hexagonal is impurities, likely to come from unreacted reactant during ZSM-5 synthesis. The addition of TiO_2 on the ZSM-5 surface retains the morphology of its forming material, namely hexagonal. The existence of this impurities makes it difficult to detect TiO_2 existence on the SEM image of the resulting composite, as shown in figure 2 c,d and e, so EDX analysis is needed.

Table 1. EDX results of TiO_2/ZSM-5 composite sample with variation of TiO_2 percent weight

Sample	**% wt**			
	Si	Al	O	Ti
2.5% TiO_2/ZSM-5	52.51	3.10	43.57	0.83
5% TiO_2/ZSM-5	45.31	2.69	49.95	2.04
10% TiO_2/ZSM-5	51.37	2.48	41.06	5.10

EDX analysis results are shown in table 1. Some amount of titanium elements in the composite sample is detected. When 2.5% weight of titanium precursor added, 0,83% weight of titanium element found in the composite sample. If the amount of titanium precursor doubled, the amount of titanium element in the composite sample also doubled. From table 1, it can conclude that the higher amount of titanium precursor added, the higher amount of titanium elements found in the composite sample.

IOP Conf. Series: Materials Science and Engineering **588** (2019) 012037 doi:10.1088/1757-899X/588/1/012037

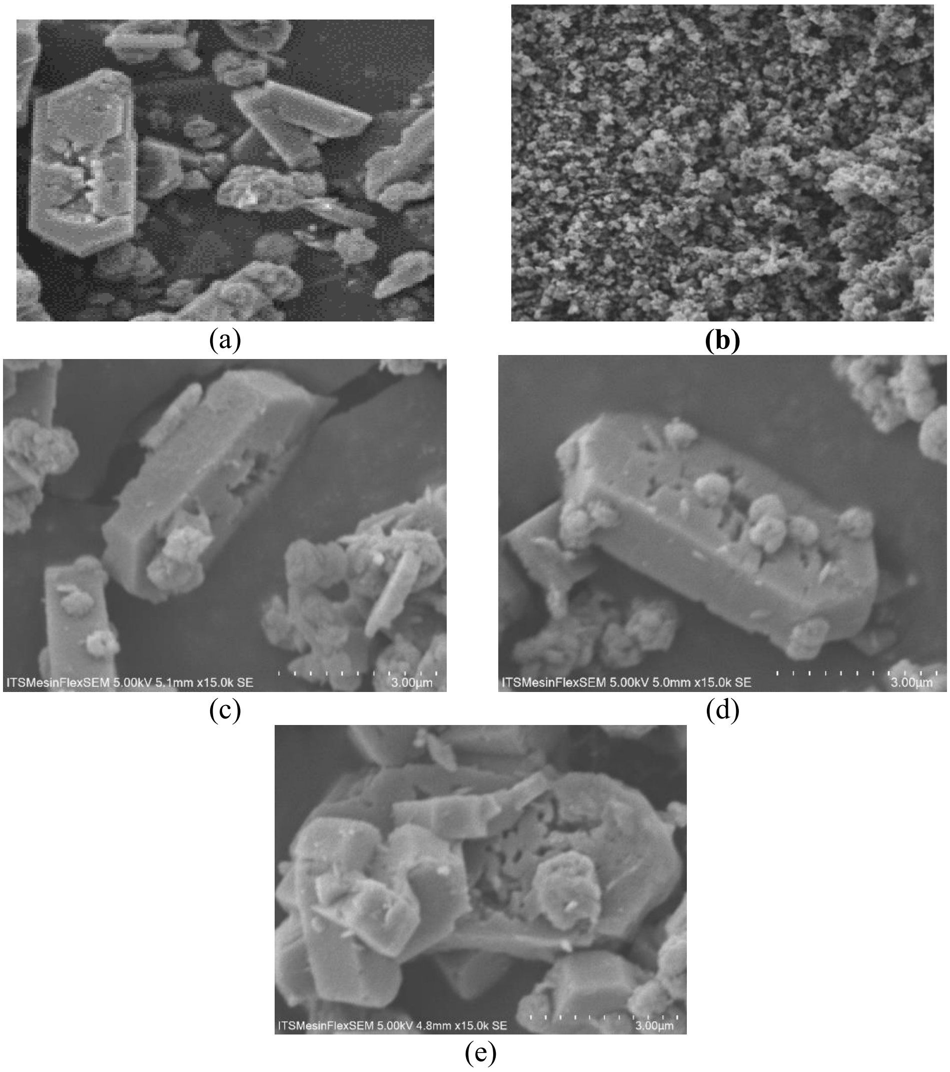

Figure 2. SEM image of a) commercial ZSM-5 b) commercial TiO_2 c) 2.5% TiO_2/ZSM-5 composite sample d) 5% TiO_2/ZSM-5 composite sample and e)10% TiO_2/ZSM-5 composite sample

3.3. Nitrogen adsorption-desorption isotherms

Addition TiO_2 on the ZSM-5 surface increases the surface area of the composite than ZSM-5 pure. However, increasing in TiO_2 content resulting in a decrease in the specific surface area of TiO_2/ZSM-5 composites, as presented in Table 2. It is possible that the solids of TiO_2 formed outside the zeolite micropore allow some parts to cover the zeolite pore thereby reducing the surface area and zeolite porosity [8].

Table 2. Specific surface area of ZSM-5 and TiO_2/ZSM-5 composites (2.5; 5 and 10%)

Sampel	S_{BET} (m^2/g)
ZSM-5	324,76
2,5% TiO_2/ZSM-5	336,31
5% TiO_2/ZSM-5	332,76
10% TiO_2/ZSM-5	327,23

4. Conclusion

TiO_2/ ZSM-5 composite have been successfully synthesized from Titanium (IV) Isopropoxide and ZSM-5 precursors via the sol-gel method. The results from X-Ray Diffraction analysis revealed that the peak showed the presence of TiO_2 anatase in sample 2.5;5; and 10% TiO_2/ZSM-5 composite. The increasing effect of Titanium precursors to TiO_2/ ZSM-5 composite carried out agglomerates on external surface of ZSM-5 as seen in SEM which was supported by surface area data from BET.

Acknowledgments
This work was financially supported by the ITS Local Grand Program 2018.

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