The Effect of Ratio Zeolite and TiO$_2$ Toward the Particle Size of Zeolite/TiO$_2$ Composites

S E Putri$^1$ and S Side$^2$

$^1,^2$Chemistry Department, Mathematics and Natural Sciences Faculty, Universitas Negeri Makassar, South Sulawesi, Indonesia

Email : ekaputri Chem@unm.ac.id

Abstract. The study aimed to determine the effect of ratio zeolite and TiO$_2$ toward the particle size of zeolite/TiO$_2$ composites. The raw material used was natural zeolite of South Sulawesi. Zeolite acts as a support catalyst of TiO$_2$ synthesized using impregnation method. The ratio of zeolite:TiO$_2$ (w/w) was 3:1; 3:1.5; 3:2; 3:2.5 and 3:3 mixed with ethanol, then calcined at 500 °C for 5 hours. The powder of zeolite/TiO$_2$ composites characterized by X-Ray Diffraction (XRD) and calculated the particle size using Debye Scherer equation. The results showed that the zeolite phase contained in zeolite/TiO$_2$ composite is modernite and TiO$_2$ catalyst phase is anatase with a tetragonal structure. The average particle size of composites increased with the increasing amount of catalyst impregnated. The smallest average size occur at zeolite:TiO$_2$ of 3:1 with 42.86 nm and the largest average size occur at 3:3 with 52.98 nm.

1. Introduction

One of the most widely practiced waste treatment today is photodegradation process. This process requires a catalyst with a semiconductor photocatalyst such as ZnO, SnO$_2$, WO$_3$, Fe$_2$O$_3$ and TiO$_2$. TiO$_2$ semiconductors are the most effective photocatalysts compared to other photocatalysts because they have the largest band gap energy, which is 3.2 eV, where a large band gap energy will result in a larger active surface area resulting in more effective photoactivity [1]. Another advantage is its affordable, non-toxic, so that it is environmentally friendly, good stability to photons, and high photocatalyst activity which is very good in showing its photodegradation activity [2]. This is also supported by research of Chitose, et.al. (2003) [3] reported that the degradation of phenol solutions is accelerated by using TiO$_2$ catalyst.

Titanium dioxide has low adsorption ability, so its photocatalytic efficiency is low. The use of TiO$_2$ also needs to be increased because if we only use TiO$_2$ it will cause sintering (clumping) of metal atoms due to the agglomeration of metal atoms, thereby reducing the surface area. TiO$_2$ activity as a photocatalyst material still has weaknesses due to its small surface area of 9.492 m$^2$/g [4] so that the capacity in the photodegradation process is small. The effectiveness of the TiO$_2$ photocatalyst can be increased by adding a carrier to the catalyst which increases the surface area of the catalyst.

According to Kautsar, et.al. (2013) [5] the photocatalyst activity of TiO$_2$ can be increased through impregnation on supporting materials that have high adsorption capabilities. Zeolite has a very high
adsorption capacity compared to other porous materials, bentonite and also activated carbon. Thus, zeolite is the most effectively used as a support material to become zeolite/TiO$_2$ composites [6]. Zeolite can be used as supporting material because it is a natural material that has a porous surface with a large surface area that allows for higher absorption of molecules [7]. Preparation and characterization of zeolite/TiO$_2$ composites, it was found that the TiO$_2$ content increased from 0.26% in zeolite to 2.80% in zeolite/TiO$_2$ composites; specific surface area from 19.57 m$^2$/g for zeolite to 67.96 m$^2$/g; total pore volume from 20.64 x 10$^{-3}$ mL/g to 49.56 x 10$^{-3}$ mL/g; and a decrease in the mean pore radius from 21.10 Å to 14.58 Å in zeolite/TiO$_2$ composites [8].

In addition, G. Liao et al. (2018) [9] also studied the characteristics of zeolite/TiO$_2$ composites for their ability as photodegradation. It shows that TiO$_2$ particles disperse on the surface of a photocatalytic cement-based material (PCM) homogeneously and provide abundant active sites for photocatalytic reactions. Compared to a normal photocatalytic cement-based material (NPCM), the TiO$_2$ content of a PCM is lower and its photocatalytic efficiency is higher. This research will examine how the effect of the ratio zeolite and TiO$_2$ toward the particle size of zeolite/TiO$_2$ composites.

2. Methodology

2.1 Synthesis of zeolite/TiO$_2$ composites

A number of zeolites that have been activated by HCl are mixed with TiO$_2$ with a ratio of zeolite:TiO$_2$ in w/w (g), namely 3:1; 3:1.5; 3:2; 3:2.5; 3:3. Then, the mixture was added with 16 mL ethanol and stirred for 5 hours. Then dried in an oven at a temperature of 120 ºC for 5 hours. After drying, crushed and sieved to 100 mesh size, then calcined at a temperature of 500 ºC for 5 hours.

2.2 Characterization of zeolite/TiO$_2$ composites using XRD

Zeolite/TiO$_2$ composites with various compositions were characterized using XRD to identify phase, crystal structure, and particle size of the zeolite/TiO$_2$ composite. Measurements by Cu-Kα radiation at 40 Kv and a current of 30 mA. The X-ray diffraction pattern represents the intensity of the diffraction peaks as a function of 2θ angle over the 10-60° range. The data obtained from characterization with XRD were analyzed using match method to obtain a diffractogram that would be compared with the JCPDS of TiO$_2$ and zeolite standards to determine the characteristics of zeolite/TiO$_2$ composites.

3. Results and Discussion

3.1 Synthesis of zeolite/TiO$_2$ composites

Zeolite activation is carried out by a chemical method using acid, which functions to remove impurities that cover the zeolite pores so that the zeolite pores are more open. In the activation process using hydrochloric acid (HCl) solution, a dealumination process occurs in the zeolite framework which aims to increase the Si/Al ratio. Activation results obtained zeolite which is light green in color. The activated zeolite was characterized using XRF to determine the composition of the zeolite constituent, shown in the results of the study before [10].

Based on the results of [10] research, it can be seen that the metal oxide composition has decreased and there is an increase in the Si/Al ratio, but it is not significant. The increase in the Si/Al ratio after activation indicates the occurrence of dealumination at the active Al-OH and Si-O-Al sites, with the release of Al from the active Si-O-Al site will cause rearrangement of Si-O-Si from outside the frame, causing the The composition of Si in the framework will increase and the metal oxide content decreases due to ion exchange between cations from zeolites and protons from HCl [11]. Reaction between zeolite and HCl showed in Fig. 1.
Figure 1. Reaction between zeolite and HCl

The activation process causes the H⁺ ions produced from the HCl decomposition reaction to break down the Al atomic bonds in the zeolite structure and also removes the balancing cations in natural zeolites (Na, Mg, Ca, Br). The H⁺ ion will break down the Al atomic bonds because the dissociation energy of the Al-O bond (116 kcal.mol⁻¹) is much lower than the dissociation energy of the Si-O bond (190 kcal.mol⁻¹), so the Al-O bond is much easier decomposed compared to Si-O [12]. Meanwhile, the Cl⁻ ion produced from the decomposition reaction has a high electronegativity so that it easily binds to large valent cations such as Si⁴⁺ and Al³⁺. However, Cl⁻ ions will tend to bond with Al³⁺ because the electronegativity of the Al atom is smaller than the Si atom.

The zeolite/TiO₂ composite was synthesized by mixing the activated zeolite with variations in weight of TiO₂, namely zeolite: TiO₂ of 3:1; 3:1.5; 3:2; 3:2.5 and 3:3 by impregnation method using ethanol as solvent. The result of the synthesis produces a solid that is getting whiter as the amount of TiO₂ increases which is followed by a calcination process at a temperature of 500 °C to clean the pores of TiO₂ particles that are not properly attached to the zeolite which produces a brownish white powder after calcination. The purpose of calcination is to remove water molecules and organic impurity compounds that are still present in the zeolite, so that the zeolite surface area will be even greater.

3.2 Characterization of Zeolite/TiO₂ Composites using XRD

The results of zeolite/TiO₂ composites synthesis with various compositions were analyzed using XRD to identify the crystalline phase, the content, and particle size of zeolite/TiO₂ composite. The diffractogram of the results of sample analysis using XRD can be seen in Fig. 2.

Figure 2. Diffractogram of XRD analysis of zeolite/TiO₂ composite
Based on the interpretation of zeolite/TiO$_2$ composite diffractogram in Fig. 2, the XRD characterization results show typical peaks of the anatase phase from TiO$_2$ with the highest peak intensity at position 2θ, each of the composition variations are 25.292°; 25.307°; 25.286°; 25.346°; 25.294 respectively with a miller index (101), which is in accordance with the TiO$_2$ diffractogram which also shows the typical upper phase TiO$_2$ peaks, 20 position at 25.291° and it is accordance with the database of Joint Committee On Powder Diffraction Standards (JCPDS number 21-1272) which the upper phase TiO$_2$ diffraction pattern 20 position is at 25.281°.

It also shows the typical peaks of the modernite phase zeolite with the highest peak intensity at the value of 2θ for each variation of the composition respectively 29.411°; 29.443°; 29.432°; 29.460°; 29.439° which has been in accordance with the zeolite diffractogram which also shows the peaks. The typical peak of modernite type zeolite, 20 position is at 29.417° and also conforms to the modernite zeolite standard (JCPDS number 06-0239) which the diffraction pattern of the modernite phase zeolite, 2θ at 29.43°. The presence of an upper phase TiO$_2$ in the composite shows that the synthesis of zeolite/TiO$_2$ composites is successful, also supported by the anatase phase TiO$_2$ structure data in Table 1.

Based on Table 1, which all phases in each composition have a tetragonal structure according to the data of TiO$_2$ structural and also according to the data (JCPDS number 211272) with lattice parameters $a = b = 3.785$ Å, $c = 9.513$ Å. This is similar with the results of research before which resulted TiO2 catalyst phases in anatase (85%) and rutile / brookite (15%) in zeolite/TiO$_2$ composites [13].

The particle size of zeolite/TiO$_2$ composites was calculated using Debye Scherrer’s formula:

$$D = \frac{0.98 \lambda}{\beta \cos \theta}$$

where 0.98 was a constant value known as a shape factor, $\lambda$ was the wavelength of the X-rays and taken as 0.154 nm, $\beta$ was the FWHM (full Width at half maximum) of the diffraction peaks and $\theta$ was the diffraction angle.

| Variation | Structure | Lattice parameter |
|-----------|-----------|-------------------|
| TiO$_2$   | Tetragonal | $a=b=3.785022$ Å, $c=9.512263$ Å |
| 3:1       | Tetragonal | $a=b=3.786624$ Å, $c=9.513763$ Å |
| 3:1.5     | Tetragonal | $a=b=3.789870$ Å, $c=9.517960$ Å |
| 3:2       | Tetragonal | $a=b=3.788351$ Å, $c=9.525439$ Å |
| 3:2.5     | Tetragonal | $a=b=3.786629$ Å, $c=9.513950$ Å |
| 3:3       | Tetragonal | $a=b=3.787617$ Å, $c=9.515924$ Å |

The results of zeolite/TiO$_2$ composites particle size are shown in Table 2.

| Zeolite : TiO$_2$ | 2-Theta (°) | FWHM (deg) | Particle Size (D) (nm) | The average Particle size (nm) |
|-------------------|-------------|------------|------------------------|-------------------------------|
| 3:1               | 25,292      | 0.195      | 43.32                  | 42.86                         |
|                   | 25,637      | 0.222      | 37.47                  |                               |
|                   | 29,411      | 0.176      | 47.81                  |                               |
| 3:1.5             | 25,307      | 0.202      | 40.77                  | 44.09                         |
|                   | 25,653      | 0.195      | 42.01                  |                               |
|                   | 29,443      | 0.169      | 49.51                  |                               |
| 3:2               | 25,286      | 0.232      | 35.55                  | 49.06                         |
|                   | 29,432      | 0.166      | 51.35                  |                               |
|                   | 48,018      | 0.151      | 60.28                  |                               |
Based on Table 2, it can be seen that the more TiO$_2$ content in the zeolite, the larger the particle size will be formed. It is because the higher of number TiO$_2$ particles in the zeolite will allow the catalyst sintering (clumping) of metal atoms due to the agglomeration of metal atoms and then form a large molecule. The smallest average size occurs at zeolite:TiO$_2$ of 3:1 with 42.86 nm and the largest average size occur at 3:3 with 52.98 nm. Besides having an effect on particle size, the composition of composites also affects the pore size of the synthesized composites [8].

The effect of composite composition on particle size has never been studied before, however, the particle size of the composite is very influential on the characteristics of composite and the performance of the catalyst as a photocatalyst. Previous research has examined the effect of composite particle size on characteristics in the form of microstructure [14], morphology [15], mechanical properties [14]–[16], and thermal properties [16]. Thus, it is hoped that the resulting data can become a reference for other researchers in applying zeolite/TiO$_2$ composites to the photodegradation process.

4. Conclusions
Based on the research results, it can be concluded that the zeolite phase contained in zeolite/TiO$_2$ composite is modernite and TiO$_2$ catalyst phase is anatase with a tetragonal structure. The average particle size of composites increased with the increasing amount of catalyst impregnated. The smallest average size occur at zeolite:TiO$_2$ of 3:1 with 42.86 nm and the largest average size occur at 3:3 with 52.98 nm.

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