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Effects of Molar Ratio on the Synthesis and Characterization Nanocluster TiO_2-SiO_2 with Induced Copolymer Chitosan by Sol – Gel.

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ABSTRACT

Nanocluster synthesis of TiO_2-SiO_2 with induced copolymer chitosan can be done through the process of hydrolysis and condensation with the sol-gel method. This study aims to optimize the synthesis process, dispersion, and surface functionalization of titanium dioxide that will be applied as a photocatalyst. Chitosan is a copolymer compound having a functional group -OH and -NH_2 that can facilitate the dispersion of TiO_2 on SiO_2 surface in order to obtain nanocluster TiO_2-SiO_2, evenly distributed, anatase structure. Product nanocluster TiO_2-SiO_2 powder, from the results of FT-IR characterization provided information that there stretching and bending vibrations of the interaction of Ti-O-Si in the fingerprint region 1100-950 cm^{-1}. X-ray diffraction analysis showed that the molar ratio between Ti : Si (1 : 1; 2 : 1 and 3 : 1) and chitosan (1 : 10; 1 : 5 and 1 : 3) gives a different effect on the growth of crystallinity of TiO_2-SiO_2 at temperature 500 ^{0}C. SEM-EDX analysis showed that the addition of chitosan acts as a template steering pore on the surface of TiO_2-SiO_2, when correlated with the data analysis shows semi-quantitative EDX element N of chitosan is still stable at calcination temperature of 500 ^{0}C during 3 hour due to the SiO_2.

Keywords: TiO_2-SiO_2; Nanocluster; Copolymer; Chitosan; Molar ratio ; Characterization

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INTRODUCTION

Sol-gel process is a chemical synthesis method which has been widely used for the synthesis of a number of materials with chemical properties that are different, such as, ceramic glass, magnet and catalyst. This method can control the composition, grain morphology, homogen, and the crystal phase structure of the resulting material (Blanchandara, *et al*., 2010 and Linacero, *et al*., 2006). For the technological developments in the synthesis of sol-gel, precursor material is used as a raw material that can be modified in such a way, in order to obtain homogeneous, un-even distribution of particles on the surface. Therefore this method is widely used in the synthesis of the material to be applied as a catalyst (Xin Zhang, 2010 and Restu, *et.al.,* 2012).

TiO_2 are semiconductors compounds, that can serve as a catalyst oxidation of some organic compounds, non-toxic and inert (Lu, *et al*., 2010; Hung *et al*., 2007). More applicable to the tropical environment of the application of TiO_2 is determined from morphologic texture, which is strongly associated with the surface area, crystalline phase structure, the size of the nanocrystal. This oxide has a low surface area that required a method to design the morphology of nanocluster TiO_2-SiO_2 through the formation of 0-50 nm in size, large surface area. Size of the material will affect the physicochemical properties, optical properties and catalytic properties of a catalyst (Hu, *et al.,* 2012).

Modification of physical and chemical properties of TiO_2 is an interesting research and mostly done by several researchers at this time, such as modifying the properties of TiO_2 catalyst with the addition of secondary semiconductor SiO_2 on TiO_2 matrix, is expected to improve the performance of TiO_2 catalysts. SiO_2 has high mechanical properties, porosity, heat stable, and the great dispersion of the TiO_2, (Axix, *et al.*, 2009). Rilda, *et. al.,* (2008) reported that, when silica is dispersed in TiO_2, the interaction between TiO_2 and SiO_2 can enhance the stability of anatase crystalline phase structure at high temperatures up to the critical temperature of the phase stability. (Lee *et al.,* 2007; Zayim *et al*., 2004; Chao *et al*., 2003). Modification of TiO_2 with the addition of dopants from the transition group consisting of a single ion and multiple ion 2 and 3 can modify the size and morphology of the surface of TiO_2, surface area (45-71) m^2/g, the titania product has been applied as a compound for inhibition of growth of several microbial pathogens.

This study aimed to synthesis of nanocluster TiO_2-SiO_2, anatase crystalline structure with sol-gel method through the induced of chitosan copolymer as a template pore. The chitosan template function to facilitate dispersion of TiO_2 on SiO_2. Chitosan will modify the microstructure of the gel and increase the porosity of the TiO_2-SiO_2 evenly. Texstur morphological differences TiO_2-SiO_2 as the effects associated with the addition of chitosan copolymer characterization of FT-IR, XRD, SEM – EDX and PSA.

MATERIAL AND METHODS

Synthesis of TiO_2-SiO_2Powder

Sol prepared by hydrolysis of a mixture of TIP and TEOS in isopropanol solvent with TIP and TEOS molar ratio (1 : 1, 2 : 1 and 3 : 1), HCl is used as a catalyst and additive DEA

with the molar ratio TIP: DEA = 1 : 2. Mixed sol in alkalinity to pH = 10 by addition of NH_4OH and stirred for 8 hours at room temperature. Condensation and hydrothermal processes carried out at a temperature of 110-120^oC for 15 hours to obtain a gel. Then the gel was calcined for 3 hours at a temperature of 500^oC in nitrogen furnace (Thermolyne 1300 Furnace) to obtain TiO_2-SiO_2 powder.

Synthesis of TiO_2-SiO_2/Chitosan

Sol was prepared from a mixture of TIP and TEOS hydrolysis in the solvent isopropanol, HCl is used as a catalyst and additive DEA is the molar ratio (TIP: DEA = 1: 2) as a mixture of A, stirred until homogeneous. Mixture B composed of chitosan dissolved in 5% acetic acid, stirred until homogeneous. Mixture B was added to a mixture with molar ratio of chitosan on TiO_2 (1 : 10, 1 : 5, and 1 : 3), pH = 10 by addition of NH_4OH and then stirred for 8 hours at room temperature until homogeneous, then continued the process of gel formation through condensation and hydrothermal process at a temperature of 110-120^oC for 15 hours. Gel calcined at 500 ^oC for 3 hours in the furnace to obtain TiO_2-SiO_2/chitosan powder.

Characterization

Physical characterization of TiO_2-SiO_2/Chitosan powder by using FT-IR (Jasco 460), for the identification of functional groups of the interaction between the raw material in the fingerprint region 4000-400 cm^{-1} using KBr pellet technique, characterization of surface texture all samples were observed with SEM - EDX (JEOL JSM 6360 LA) and crystalline phase identification with X-ray Diffraction (XRD Shimidzu 7000 with Cu-Kα radiation source), particle size distribution identified by PSA.

RESULTS AND DISCUSSION

Optimization Synthesis of TiO_2 with SiO_2 addition

Silica (SiO_2) is a metal oxide that has several advantages to modify the performance of TiO_2 catalysts functions such as high mechanical properties, large surface area, heat stable, and the great dispersion of the TiO_2. Variation of the molar ratio between Ti and Si aims to observe how it affects the morphology of the resulting crystals. In this study the molar ratio of Ti and Si varied 1 : 1, 2 : 1 and 3 : 1. Patterns of FT-IR indicate that the presence of functional groups that appear in the fingerprint region such as shown in Figure 1, from the pattern of FT-IR showed an interaction between chitosan on SiO_2 and TiO_2, which appeared in the fingerprint region intensity 425.2 cm^{-1} and 461.9 cm^{-1} to O-Ti-O. Chemical interactions between SiO_2 and TiO_2 are shown in the absorption band at wave number 1105 to 950 cm^{-1}. Differences of the three comparison groups is no wave numbers 1105 - 950 cm^{-1}, where the smaller the number of comparisons that are added to Si, the greater the intensity of the region, Ti : Si with a ratio of 3 : 1 greater than 2 : 1 and 1 : 1 .

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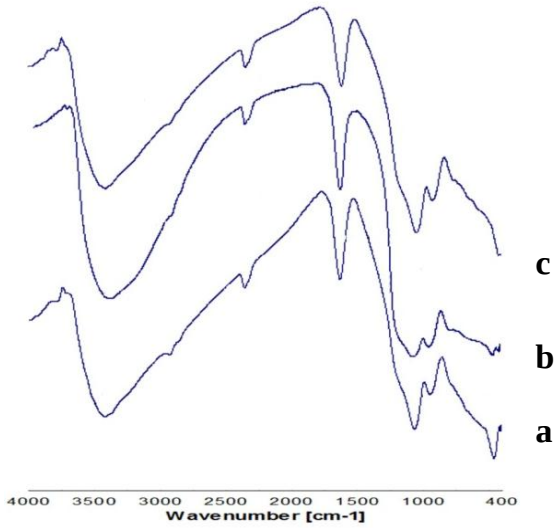

Figure 1. FT-IR Pattern of TiO_2-SiO/Chitosan 20%, Gellation 15 hours Calcination 500^{0}C for 3 hours with a Variation of The molar ratio of Ti : Si, a.3: 1, b. 2:1, and c. 1:1

As shown in Figure 2 TiO_2-SiO_2/chitosan is 2θ = 25.17^o. It is based on data JCPDS No. 03-065-5714. SiO_2 has amorphous structure. More over, the addition of SiO_2 on TiO_2 structure tends to transform into an amorphous phase if increasing the amount of SiO_2. Besides the advantages of SiO_2 is able to increase the thermal stability of TiO_2, so it is necessary to prevent the transformation of the crystal structure that is metastable anatase TiO_2 to rutile structure, at high calcination temperature heating. Based on the research Balachandaran (2010), anatase TiO_2 is stable at calcination temperatures below 500^{o}C, the temperature at the top of rutile TiO_2 formed.

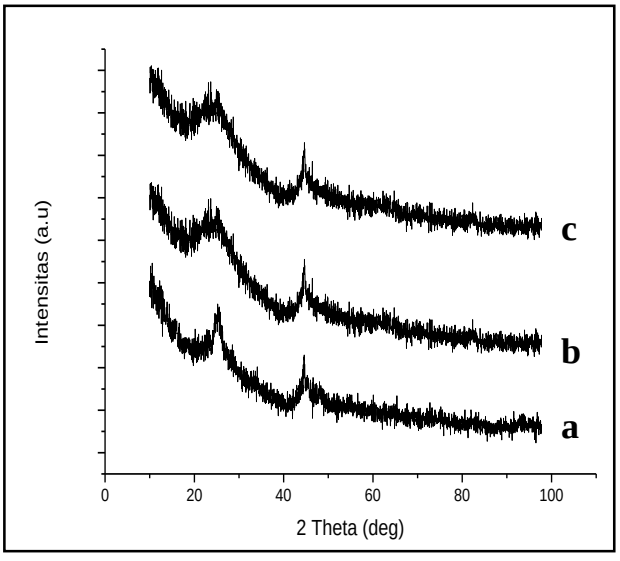

Figure 2. XRD Patterns of TiO_2-SiO_2/Chitosan 20%, Gellation 15 hours Calcination for 3 hours at a Temperature of 500^{0}C by Variations in The molar ratio of Ti: Si, a.3: 1, b. 2:1, and c. 1: 1

Comparison of Ti : Si different giving patterns of different TiO_2 crystal structure, the formation of a more perfect crystals in samples with less SiO_2 composition is 3 : 1. SiO_2 effects can also slow the growth of crystals of anatase TiO_2 at 500^{o}C calcination

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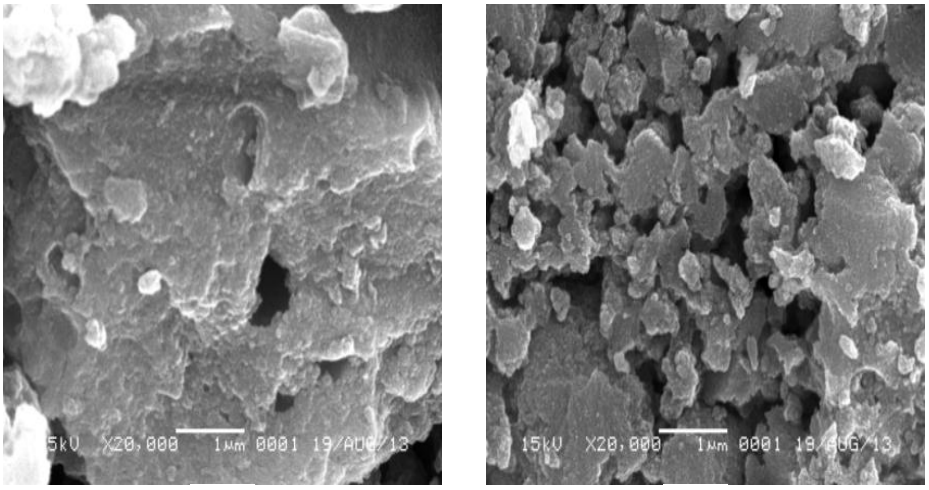
temperature. So as to obtain a more perfect crystalline phase should be increased calcination temperature of TiO_2-SiO_2-chitosan, while the effect of the addition of chitosan on morphology of TiO_2-SiO_2 also have a tendency of giving an amorphous phase.

Pattern in Figure 3 depicts SEM surface morphology of TiO_2 products modified with the addition of SiO_2. TiO_2-SiO_2 surface provides porosity on the surface of TiO_2. If the molar ratio SiO_2 to TiO_2 contribution equal to a given pore on the surface of TiO_2-SiO_2 more than 3 : 1 ratio of Ti to Si.



a **b**

Figure 3. SEM Patterns of TiO_2-SiO_2/Chitosan 20%, 5 hours Gellation, Calcination 500°C, over 3 hours of a) 1:1 and (b) 3:1.

In the comparison of Ti : Si 3 : 1, showing the growth of TiO_2-SiO_2 crystals is more perfect than the 1 : 1 ratio where the Ti : Si 1 : 1 with the tends amorphous surface. SEM analysis of the results in Figure 3, it can be assumed that the chitosan as template pore structure on the surface of TiO_2-SiO_2, the effect of chitosan involved during the process started gellasi, and decomposition will occur at calcination temperatures higher than 300^0C, as EDX pattern in Figure 3, From the EDX analysis it can be observed that SiO_2 can serve to inhibit chitosan degraded at a temperature of 500^0C. Information obtained from EDX analysis that the process at a temperature of 500^0C calcination, N elements of the compound chitosan was detected.

From the SEM pattern in Figure 3 shows that the variation ratio TiO_2-SiO_2/chitosan Ti : Si 1: 1 has percentage elements C = 4.85%, N = 4.49%, Si = 33.93% and Ti = 58.35%. While the ratio of 3 : 1, the percentage of the elements C = 10.08%, N = 2.89%, Si = Ti = 19.88% and 65.55%. Seen that increasing the ratio of Ti : Si, Ti intensity increased and also the larger crystal size.

TiO_2-SiO_2/chitosan material resulting from modifications made have managed to get the product to the surface morphology of nanoporous TiO_2-SiO_2/kitosan are distributed evenly like the pattern in Figure 4. By dispersing SiO_2 on TiO_2, SiO_2 and TiO_2 surface coat will provide a porous surface, as observed in the SEM image.

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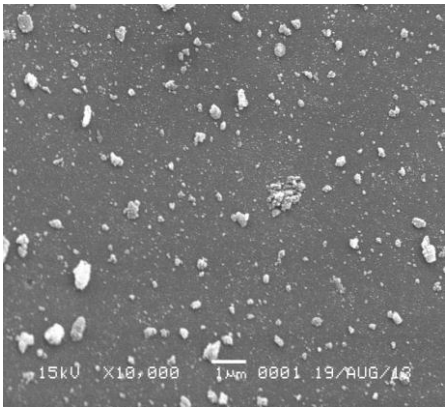

Figure 4. SEM Patterns of TiO_2-SiO_2 3 : 1 without Chitosan, Gellation hours, 500°C Calcination, 3 hours.

SEM pattern in Figure 4 shows a comparison of Ti : Si 3 : 1 without the addition of chitosan, to control how the comparative effects of adding chitosan copolymers for the synthesis of TiO_2-SiO_2. SEM of the pattern can be observed that chitosan does not happen without a directional pore formation on TiO_2-SiO_2 surface, so in this case it can be assumed that chitosan acts as a pore template directional printing on the surface of TiO_2-SiO_2.

Effect of chitosan could also affect the crystallinity of TiO_2-SiO_2/chitosan more perfect, this fact can be seen from the results of EDX analysis. From the EDX pattern shows that the TiO_2-SiO_2 without chitosan. Seen that without the lower chitosan crystal growth, increasing the intensity of Ti.

SEM patterns can be correlated with the pattern of PSA in Figure 5 to observe the particle size distribution, which of the characterization by XRD patterns show crystalline phases are not show on the intensity ratio of Ti : Si 1 : 1, thus constrained in determining the crystal size using Scherer equation, and required an increase in the calcination temperature so that the process can be more perfect crystallization. PSA date can be informed that there are differences in the particle size distribution of the molar ratio of Ti : Si = 3 : 1 is larger than Ti : Si at ration1 : 1. Therefore it can give you an idea that there are effects of the molar ratio of Ti and Si in modified morphology TiO_2-SiO_2/chitosan.

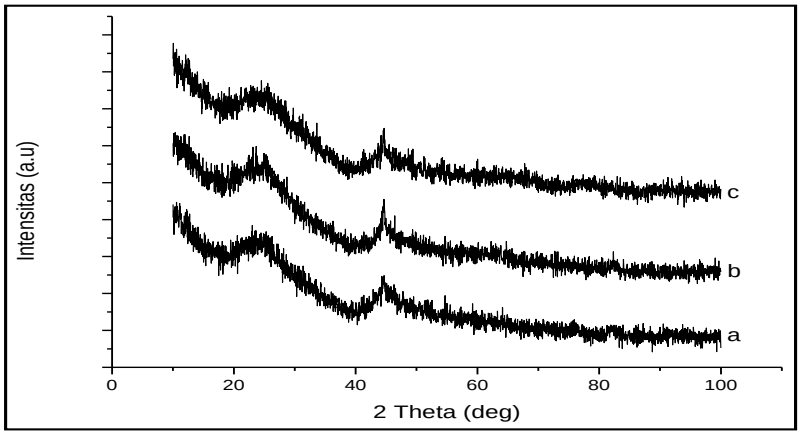

Figure 5. XRD Patterns of variation Concentration Chitosan (a) 10% (b) 20% (c) 30%) in the synthesis of TiO_2-SiO_2 (2 : 1), gellasi 15 hours, 500°C calcination temperature, for 3 hours.

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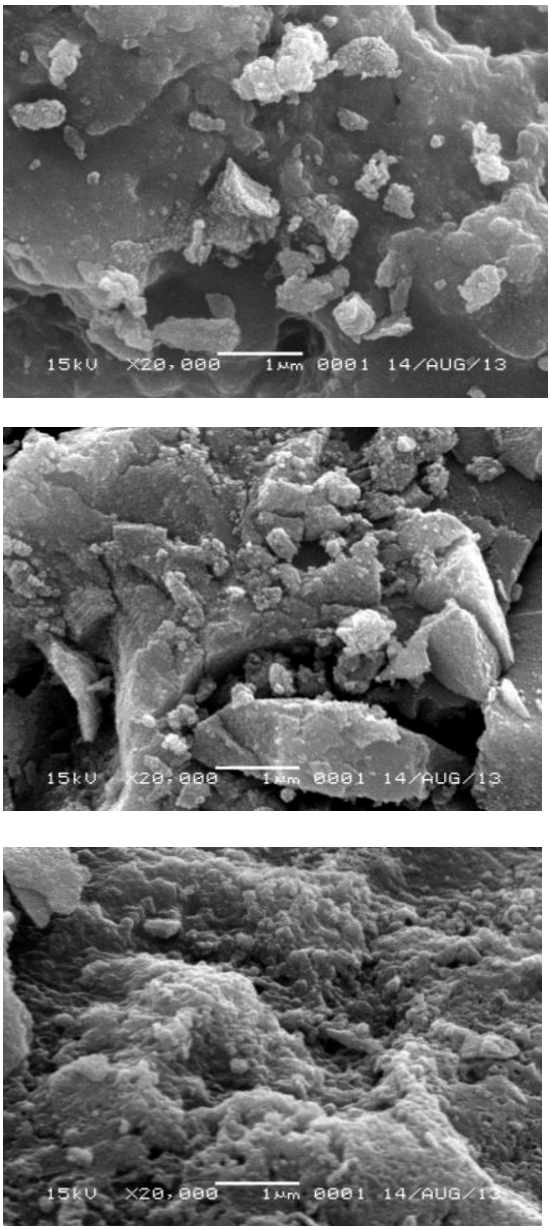
Effect of chitosan concentration variation in the synthesis TiO_2-SiO_2/chitosan

The effect of adding different concentrations of chitosan on the crystal phase that tends to give amorphous. But of SEM patterns (Figure 6) can give an idea that by increasing the concentration of chitosan TiO_2-SiO_2/chitosan tendency for amorphous product, it can be correlated with the properties of chitosan is a copolymer of organic compounds. But at a temperature of 500^0C chitosan can contribute inorganic N is a monomer on TiO_2, it can be assumed that the stability of the chitosan may occur because of the SiO_2 coating that has a high thermal stability. To obtain the crystallization of a more perfect TiO_2-SiO_2/chitosan necessary to improve the calcination temperature. In this study, the effect of chitosan on the formation TiO_2-SiO_2/chitosan crystal size can not be determined.



a

b

c

Figure 6. SEM Patterns of Variation Chitosan (a) chitosan 10% (b) 20% chitosan (c) chitosan 30%) in Synthesis of TiO_2-SiO_2 (2:1), Gellation 15 hours, 500^oC Calcination Temperature, for 3 hours

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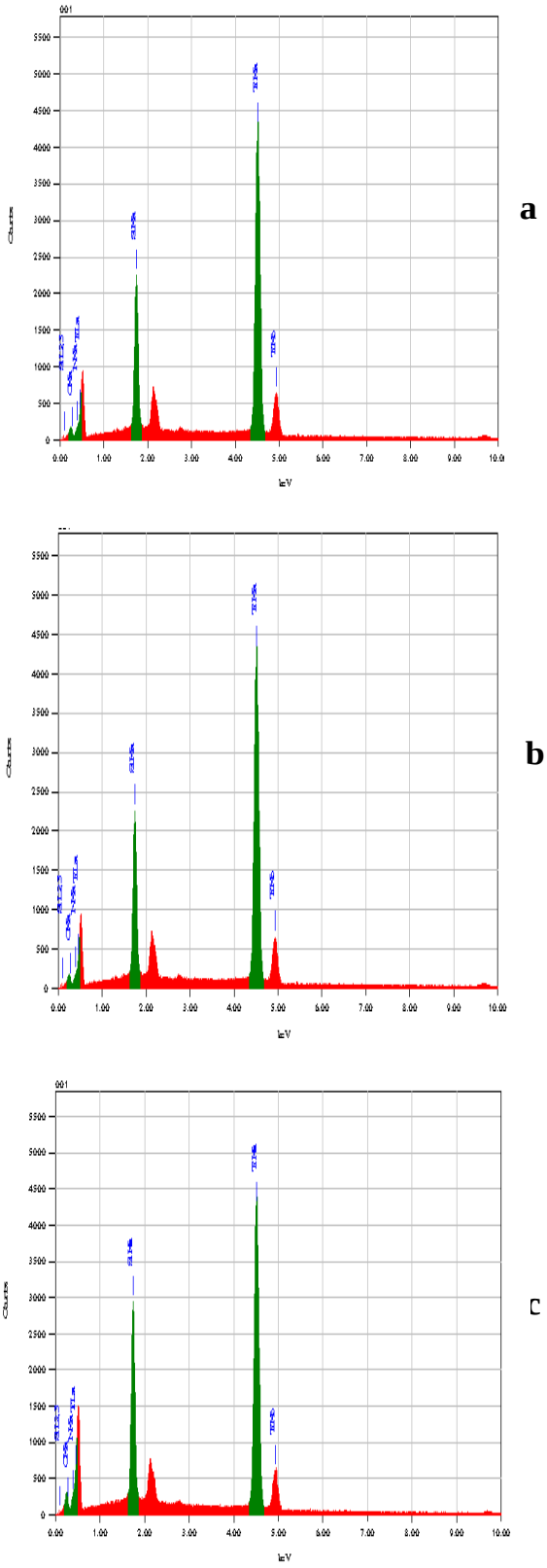

Figure 7. EDX Pattern of Variation of Chitosan (a) chitosan 10% (b) 20% chitosan (c) chitosan 30% On Synthesis of TiO_2-SiO_2 (2:1), gellation 15 hours, 500^oC Calcination Temperature, for 3 hours.

The effect of adding different concentrations of chitosan on providing XRD pattern differences are almost similar. Crystalline phase in the amorphous form of slight molar ratio of Ti and Si 2 : 1, with the calcination temperature 500^oC, for 3 hours. But the pattern of SEM

in Figure 8, can provide information that by increasing the concentration of chitosan TiO_2-SiO_2/chitosan tendency for amorphous product, it can be correlated nature of chitosan is a copolymer of organic compounds, as well as amorphous surface if the surface is coated with TiO_2-SiO_2. To obtain the crystallization of a more perfect TiO_2-SiO_2/chitosan necessary to improve the calcination temperature. In studying the effect of chitosan on the formation TiO_2-SiO_2/kitosan crystal size can not be determined. So that the data can be correlated with PSA.

From the EDX pattern (Figure 7) shows that the TiO_2-SiO_2 with chitosan concentration ratio greater Ti gives a higher intensity, so as to give an idea that chitosan plays a role in the formation of crystalline TiO_2 to be more perfect, and optimization best concentration is the concentration of chitosan with 20% . Each of these provides the chitosan composition analysis of the composition is as follows, chitosan has a 10% percentage of the elements of C = 5.88%, N = 0.42%, Si = 17.2 and Ti = 72.91%. On chitosan 20%, the percentage of the elements of C = 0.69%, N = 0.69%, Si = 18.06% and Ti = 83.69%. While at 30% the percentage of chitosan elements C = 1.89%, N; 0.95%, Si = 14.72% and Ti = 79.16%.

SEM pattern when correlated with the pattern of PSA (Figure 8) can provide information that the effect of chitosan in modifying the morphology of the particle size distribution of TiO_2-SiO_2, with the addition of chitosan particle size distribution greater than 150 µm whereas there was no dominant particle size distribution of chitosan on the percentage distribution of 50 µm.

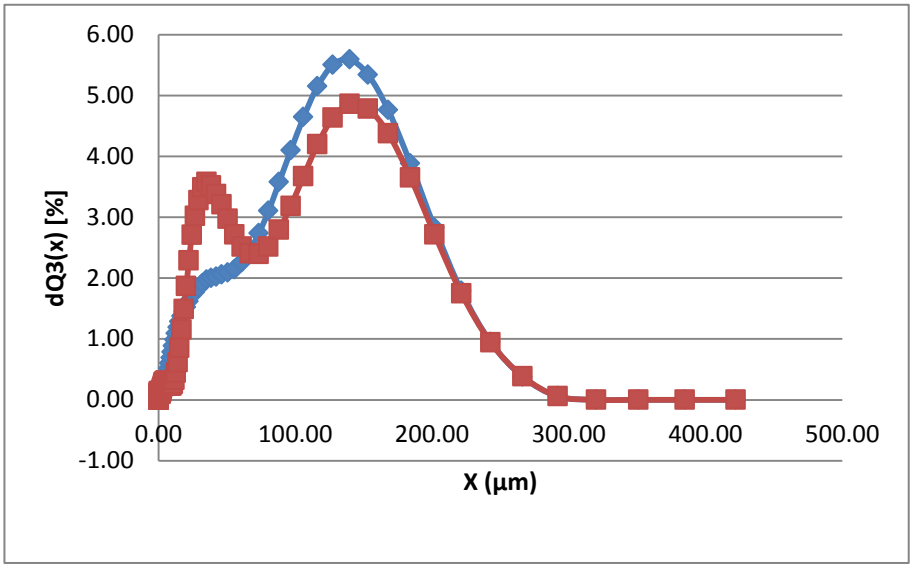

Figure 8. PSA Pattern of a. TiO_2-SiO_2 (1:1) /Chitosan 20%, b. TiO_2-SiO_2 (3:1) /Chitosan 20%, Gellation 15 hours, Calcination Temperature of 500°C, for 3 hours

CONCLUSION

Chitosan functions as a template pores and can improve the dispersion nanocluster SiO_2 to TiO_2 through the stages of the process of hydrolysis and condensation of the sol-gel. Product nanocluster TiO_2-SiO_2 powder, from the results of FT-IR characterization was obtained that the vibration occurs between Ti-O-Si in the fingerprint region 1100 - 950 cm^{-1}. X-ray diffraction analysis showed that the molar ratio between Ti : Si (1 : 1, 2 : 1 and 3 : 1)

to give different effects on the growth of crystallinity of TiO_2-SiO_2. SEM-EDX analysis showed that the addition of chitosan 20% to give a more even surface pores on the surface of TiO_2-SiO_2, and SiO_2 gives heat stability of the chitosan and TiO_2-SiO_2 at 500^0C calcination temperature.

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