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Synthesis of Titanium Dioxide (TiO_2) Fine Particle by Flame Spray Pyrolysis (FSP) Method using Liquid Petroleum Gas (LPG) as Fuel

Hendri Widiyandari[1*)], Vincensius Gunawan[2)], Susilo Adi Widyanto[3)] and Agus Purwanto[4)]

[1)]Department of Physics, Faculty of Mathematics and Natural Sciences, Sebelas Maret University
Jl. Ir. Sutami 3A Kentingan, Surakarta
[2)]Department of Physics, Faculty of Science and Mathematics, Diponegoro University
Jl. Prof. Soedarto, SH, Tembalang, Semarang
[3)]Department of Mechanical Engineering, Faculty of Engineering, Diponegoro University
Jl. Prof. Soedarto, SH, Tembalang, Semarang
[4)]Department of Chemical Engineering, Faculty of Engineering, Sebelas Maret University
Jl. Ir. Sutami 3A Kentingan, Surakarta

[*)]Coresponding author: hendriwidiyandari@staff.uns.ac.id

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Abstract

This study aims to obtain titanium dioxide (TiO_2) fine particle with a narrow size distribution by one step production via flame spray pyrolysis (FSP) using LPG (liquid petroleum gas) as a fuel source. The TiO_2 particles were synthesized from the aqueous based precursor from dissolving of titanium (IV) isopropoxide to the acidic distilled water solvent. The effect of precursor concentration on the crystalline structure, morphology and size distribution of the TiO_2 particles were systematically investigated. There were observed that the TiO_2 has a uniform spherical shape with particle size around 200-500 nm. Increasing the precursor concentration resulted in the size distribution shifted toward the bigger size. The crystalline structure of TiO_2 product showed the mixed phase of anatase and rutile and had a large specific surface area ~850,343 m^2/g.

Keywords: *flame spray pyrolysis; monodisperse; spherical shape; titania; uniform size*

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INTRODUCTION

Titanium dioxide (TiO_2) is an N-type oxide semiconductor material having an energy band gap of 3.2 eV. TiO_2 particles have been widely used as primary materials in energy converting devices such as solar cells (Jeong *et al.*, 2016) and catalysts on hydrogen production (Pan *et al.*, 2016). In addition, the particles are highly environmentally friendly photocatalyst materials that can be applied in the process of degradation of organic pollutants (Bettini *et al.*, 2015), self-cleaning process (Kim *et al.*, 2016), anti-bacterial and anti-odour (Fagan *et al.*, 2016). Research and utilization of TiO_2 particle get a lot of attention because of its very diverse applications. TiO_2 also has quite interesting properties including non-toxic, stable, abundant and relatively economical. (Kim *et al.*, 2004). Production of the TiO_2 particle is not only focused on the preparation of small size particles, but also consider several criteria such as to obtain identical or uniform sizes, identical shapes, chemical composition and identical crystal structure as well as monodisperse or non-agglomerated particles (Cao, 2004). Characteristics of the TiO_2 particles strongly affect properties of materials such as electrical, mechanical, optical, thermal and chemical properties of materials such as catalytic reaction rate.

Several methods for producing TiO_2 particulate powders have been reported, comprising sol-gel method, synthesis in the gas phase by means of electric furnace and using flame (Chang *et al.*, 2008). However, the production of TiO_2 particle with good crystalline using sol-gel method, required some advanced stages such as separation and sintering (Cushing *et al.*, 2004). The flame-assisted method is a good option due to several advantages such as high production rate, relatively cheap, and its continuous production process. In addition, this process was able to produce particulate powder in one stage and it was possible for scaling up (Strobel *et al.*, 2006). Material synthesis by flame auxiliaries is widely implemented to produce small powder particles of high purity and single-phase particles. However, utilization of a vapor-fed flame reactor is very difficult to obtain multicomponent material. Flame spray pyrolysis (FSP) is a method of particle synthesis by converting liquid droplet into solid (liquid droplet to solid conversion) (Chang *et al.*, 2008). The FSP reactor system consists of three main parts including droplet generator, reaction chamber, and particle collector. During this time, methane gas is the most commonly used as flame fuel source in the production of particle powder (Purwanto *et al.*, 2008; Bettini *et al.*, 2015). As we know, methane is highly flammable and dangerous gas that requires special handling as well as costly gas.

This study aims to produce TiO_2 powder particles in one step production by using FSP method with LPG (liquid petroleum gas) as a fuel source. LPG is a gas that is very widely used in daily life at affordable price.

MATERIALS AND METHODS

Materials

The materials used to produce TiO_2 powder particle were titanium (IV) isopropoxide (TTIP, Aldrich Chemicals, USA, purity of 97%) and nitric acid (HNO_3, Merck, Germany). All materials are used directly from the manufacturer without purification.

Preparation of TiO_2 particle

A precursor solution was prepared by slowly adding of TTIP to the solution containing 120 mL of distilled H_2O and 1.2 mL of Nitric acid under vigorously stirring. After being continuously stirred for 2 h at 30°C, the formed homogenous solution was obtained. The as-prepared solution requires 3 days for ageing process. Figure 1 shows a schematic diagram of FSP reactor for the synthesis of a TiO_2 powder particle. The precursor solution is converted to droplet using the ultrasonic nebulizer as droplet generator. The resulted droplet is then fed to the chamber reactor for evaporation process, decomposition and solidification reactions. Those reactions took place by flame assistance. The resulting particulate powder were collected on the bag filter that connected to the rotary pump as a particle collector. The chemical reactions of TiO_2 synthesis using TTIP are defined as the following:

$$Ti(OCH(CH_3)_2)_{4(l)} + 18O_{2(g)} \rightarrow TiO_{2(s)} + 12CO_{2(g)} + 14H_2O_{(g)}$$

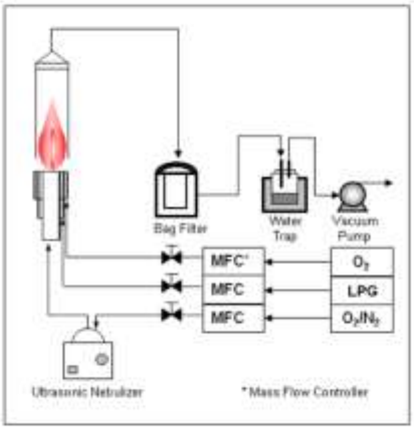

Figure 1. Schematic diagram of FSP reactor

Characterization

The powder particle was then characterized by using X-ray diffractometer (XRD, Shimadzu XRD-700, Japan) with CuKα radiation source at the wavelength, λ = 0.15406 nm to determine the crystalline properties of the material. Scanning electron microscope (SEM, JEOL JSM- 6360 LA, Japan) with electron energy at 15 ke V was applied to determine the morphological properties of the material. Surface area and pore size were determined based on Nitrogen adsorbtion-desorption testing using Bruneur Emmett Teller (BET, NOVA e-series, Quantachrome Instruments, USA) method.

RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffraction pattern (XRD) of TiO_2 particle powder prepared by the LPG-fueled FSP method. The obtained TiO_2 has a crystalline phase which is a mixture of the anatase phase and the rutile phase. The x-ray diffraction pattern data corresponds to JCPDS No. 21-1272 indicating anatase phase and JCPDS No. 88-1175 indicating the rutile phase. Increasing the precursor concentration from 0.02 to 0.07 M does not imply the change of TiO_2 crystals phase. This is possible because the small precursor concentration changes. The synthesis of the TiO_2 powder particles using the FSP method required a completely homogeneous precursor solution. Preparation of homogeneous TTIPs precursor solution can occur at low concentrations whereas at high concentrations is quite difficult to obtain. The XRD data is then processed to determine the value of the size of the crystal (τ) using the scherrer equation (1) and the results are summarized as shown in Table 1 and Table 2.

$$\tau = \frac{K\lambda}{B\cos\theta} \quad (1)$$

K is a form factor, with a value of 0.94, B is FWHM (full width at half maximum) and θ is the diffraction angle. The calculation of crystal size in the diffracted plane (101) shows that the concentration increases from 0.02 to 0.07 M, gives a tendency of increasing the size of the crystals in the anatase phase. In contrast, the results of crystal size calculations on the diffracted plane (111) show that at a concentration of 0.05 M, TiO_2 in the rutile phase has the smallest crystalline size. Calculating the size of TiO_2 crystals in this rutile phase gives the same tendency at each peak measured.

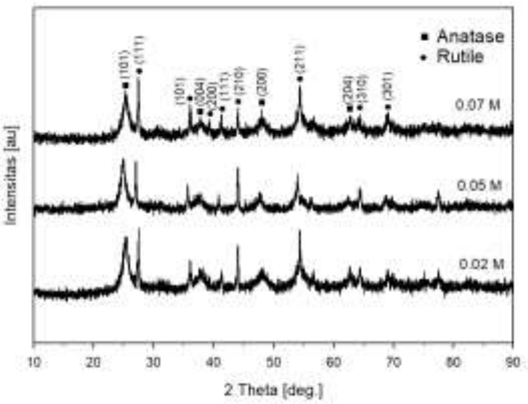

Figure 2. XRD patterns of TiO_2 synthesized by FSP using LPG fuel source at different precursor molarity.

Table 1. The crystal size calculation results in the diffracted plane (101) representing the anatase phase

Molarity (M)	2θ (deg)	θ (deg)	Cos θ	FWHM (deg)	FWHM (rad)	τ (nm)
0,02	25	12,5	0.9763	0,8900	0,0155	9,1065
0,05	25	12,5	0.9763	0,8934	0,0155	9,0718
0,07	25	12,5	0.9763	0,592	0,0103	13,690

Table 2. The crystal size calculation results in the diffracted plane (111) representing the rutile phase

Molarity (M)	2θ (deg)	θ (deg)	Cos θ	FWHM (deg)	FWHM (rad)	τ (nm)
0,02	27	13,5	0,9724	0,2305	0.0040	35.0214
0,05	27	13,5	0,9724	0.,99	0.0087	16.1772
0,07	27	13,5	0,9724	0,233	0.0040	34.6457

Figure 3 shows SEM images of TiO_2 synthesized at different precursor concentrations at 0.02, 0.05 and 0.07 M. It is confirmed that TiO_2 synthesized using the LPG FSP method has uniform shape and size. The produced TiO_2 powder particles are spherical and dense with non-agglomerated particles or as a primary particle. The size of TiO_2 particles obtained for each synthesis condition is also relatively uniform.

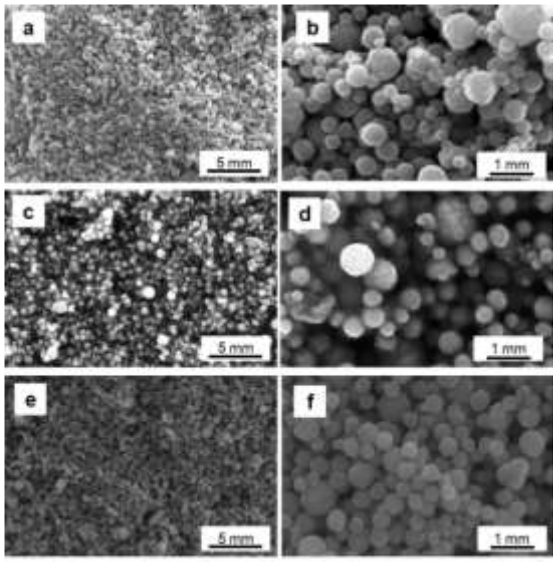

Figure 3. SEM images of TiO_2 synthesized by FSP using LPG fuel source at different precursor molarity, (a,b) 0,02; (c,d) 0,05; and (e,f) 0,07 M.

Figure 4 shows particle size distribution of TiO_2 particle. Increasing precursor concentration tends to increase the TiO_2 particle size of 0.48, 0.68 and 0.84 micrometres at the precursor concentration of 0.02, 0.05 and 0.07 M, respectively.

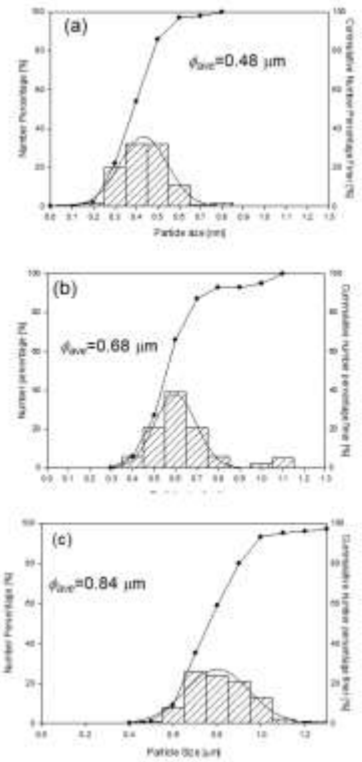

Figure 4. Particle size distribution of TiO_2 synthesized by FSP using LPG fuel source at different precursor molarity, (a) 0,02; (b) 0,05 and (c) 0,07 M.

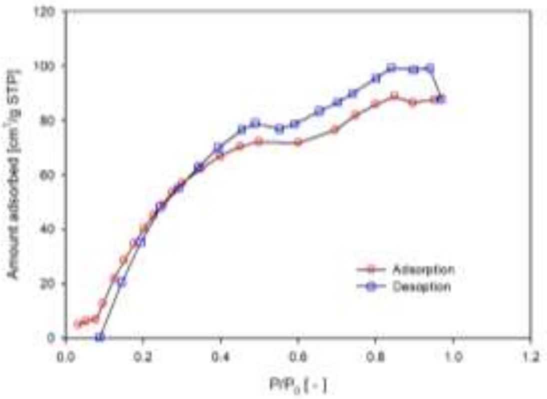

Figure 5. N_2 adsorption-desorption isotherm of TiO_2 (TTIP molarity of 0,05 M)

Figure 5 displays the result of N_2 adsorption-desorption isotherm of TiO_2 which was synthesized from a precursor at a concentration of 0.05 M. By using equation (2), we can calculate the specific surface area (S_{BET}) of TiO_2 of 850,343 m²/g. The specific surface area of TiO_2 obtained from the experimental results was larger than that of the commercial TiO_2 (TiO_2 Degussa P25) of 50 m^2/g (Tian *et al.*, 2008).

$$S_{BET} = \frac{V_m}{22414} \times L \times \sigma \qquad (2)$$

V_m is the monolayer volume, L is the Avogadro number and σ is the cross section area of the adsorbate molecule, which for σ (N_2) at the liquid nitrogen temperature is 0.162 nm^2.

CONCLUSION

The TiO_2 powder particle can be synthesized by using Flame Spray Pyrolysis (FSP) method with LPG (liquid petroleum gas) as the fuel. The obtained TiO_2 particle powder has a crystalline phase with a mixed crystalline phase between the anatase phase and the rutile phase. The obtained powder of TiO_2 particles has a uniform spherical shape, and the particles are not agglomerated or in other words are a primary particle. The particle size of the particles was slightly affected by the precursor concentration, with the mean particle size of 0.48, 0.68 and 0.84 micrometres at precursor concentrations of 0.02, 0.05 and 0.07 M respectively.

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