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Modified Sol-Gel Method in TiO_2 Fabrication for Conversion of Glucose to High-Value Chemicals

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Abstract. Glucose was successfully converted to be high-value products (acidic compounds) via photocatalytic oxidation with TiO_2. This is a new route for chemical production of high-value chemicals. The development of TiO_2 synthesis is interesting to improve the properties of photocatalysts. In this research, TiO_2 synthesized by modified sol-gel method with microwave (MW) irradiation resulted in small particles and a mixed-crystalline structure of anatase and rutile phases (28.7:65.2). The small particle sizes of TiO_2 (MW) (400 nm) influenced high glucose conversion (i.e. 67.7 % at 120 min) because of higher adsorption site of glucose. The mineralization of organic products was occurred after 15 min since pH value of solution trended to increase with increasing time.

Keywords: biomass, sugar, titanium dioxide, sol-gel synthesis, photocatalytic oxidation.

1. Introduction

Conversion of biomass to renewable chemicals has received significant attention as one of the key technologies for the sustainable society [1]. In recent years, many researchers have attempted to find ways to utilize biomass as feedstock for the production of chemicals and fuels because of its abundance and renewability [2]. In the basis of biomass, it is consisted of hydrocarbon compounds (carbon, hydrogen, and oxygen are mainly elementals) like fossil fuels, but its chemical compositions are different. Cellulose, hemicelluloses, and lignin are polymeric hydrocarbon which their structures are linear homopolysaccharide, branched heteropolysaccharide and complex three-dimensional polymer of polyphenolic substance, respectively [3]. To consider the glucose, it is abundant and is an important sugar monomer in the structure of cellulose. Recently, various processes have already been developed for biomass conversion including steam gasification, fast pyrolysis, and super critical conversion [4]-[6]. Nevertheless, these processes also require high temperature, high pressure, and high system cost to produce chemicals and fuels. Photo-catalysis is one of promising process because it can be performed under solar irradiation at room temperature and mild condition [7].

Titanium dioxide (TiO_2) has been considered to be the most attractive heterogeneous photocatalyst due to it presents the excellent photocatalytic activity, low level of toxicity, and strong oxidizing power [8]. It has been widely used for degradation of organic species in waste water, H_2 production, and dye sensitized solar cells [9]-[11]. TiO_2 can be fabricated by sol-gel method that it is easy to operate and inexpensive [12]. In addition, the photocatalytic activity of TiO_2 is depended on morphological appearances and properties such as surface area, particle distribution, crystallinity, *etc*. Thus, the aim of the present article focused on simplify modification technique to improve the properties of TiO_2 that can enhance the photocatalytic conversion of

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glucose to acidic compound products, *i.e.* glucaric acid and gluconic acid, which are high-valued organic compounds that are usually used as platform and building block molecules. The characterizations of TiO_2, photocatalytic conversion were carried out and reported.

2. Experimental

2.1. Preparation of TiO_2

Titanium (IV) butoxide (Fluka) was mixed with the same mole of acetylacetone (ACA, Sigma Aldrich). Subsequently, 80 mL of distilled water was added drop wise into the solution under stirring at room temperature follow by adding 60 mL of isopropyl alcohol. The mixed solution was kept at room temperature for 24 h to gel formation followed by drying at 80 ℃ for 24 h. The synthesized TiO_2 was pulverized into small particles, then it was calcined at 500 ℃ for 5 h. Ultrasonic assisted TiO_2 (US) was synthesized in the same manner, but the mixture solution was treated with ultrasonic (35 kHz, 320 W, Sonorex Digitec, Bandelin) for 1 h in 5 and 10 min per cycles (2 min ultrasound off between cycles) before aging at room temperature for 1 h. Similarly, the microwave assisted TiO_2 (MW) was fabricated with the same method and the mixture solution was treated under microwave irradiation (Whirlpool, 2.45 GHz, 970W) for 4 min before drying at 80 ℃ for 24 h.

2.2. Photocatalytic reaction

The 500 mL of glucose solution (1 g/L) was prepared in a mixture of distilled water and acetonitrile (10:90 v/v) and a concentration of 1 g/L of photocatalyst were transferred into borosilicate cylindrical double-walled reactor followed by continuous stirring for 30 min in dark condition for complete adsorption of glucose on photocatalyst surface. A 400 W of mercury lamp (λ_{max} = 365 nm) was used as a light source to irradiate the sample that located beside the reactor and reaction temperature was maintained by cooling water system. The 10 mL of samples were taken from the photoreactor at specified times, then it was filtrated through 0.45 μm of nylon filter to remove the photocatalyst particles before analysis. The glucose conversion was monitored by high-performance liquid chromatograpy (HPLC, Shimudzu, LC-20AD pump) equipped with a refractive index detector (Shimudzu RID-10A). Separation was performed on an Aminex HPX-87H column (300 x 7.8 mm) (Bio-Rad). The mobile phase was 5 mM sulfuric acid at a flow rate of 0.5mL/min and injection volume was 20 μL. The organic acid as products in this research was monitored by pH meter (Metrohm).

2.3. Characterizations of photocatalyst

The microstructure of the TiO_2 particles was analysed by scanning electron microscopy (SEM; JEOL JSM-6500FE). The constituent phases were determined by X-ray diffraction (XRD; RIGAKU RINT 2100) with Cu-Kα radiation (λ=0.15418 nm) at 40 kV and 30 mA. The average crystal sizes were estimated from the line broadening of X-ray diffraction reflections using Sherrer equation (1);

$$D = K\lambda / \beta cos\theta, \quad (1)$$

where D is crystallite size, K is a coefficient (0.89), λ the wavelength of the X-ray radiation and β is the full-width at half-maximum (FWHM) intensity of peak, and θ is the diffraction angle.

3. Results and Discussion

3.1. Photocatalyst characterizations

XRD patterns of calcined photocatalysts are showed in Fig. 1. All of TiO_2 photocatalysts presented 3 main peaks of anatase at 2θ of 25.4°, 37.8, and 48.1°. The TiO_2 (US) and TiO_2 (SG) photocatalysts exhibited only anatase phase and same crystallite size of 25.1 nm (see Table 1). It indicated that ultrasonic treatment did not significantly affect the crystallite size of anatase because it was low frequency (35 kHz) of ultrasonic radiation. Interestingly, TiO_2 (MW) showed the mixture of anatase and rutile (2θ = 27.5°), but the diffraction line of anatase is lower than that of TiO_2 (US) and TiO_2 (SG). There were 87% and 14% of anatase and rutile, respectively, with crystallite sizes of 28.7 and 65.2 nm, respectively. This result implied that heat treatment under microwave radiation facilitated the transformation of anatase to rutile phase. However, TiO_2 (MW) had

larger anatase-crystallite size than that of TiO_2 (US) and TiO_2 (SG). SEM images of TiO_2 (SG), TiO_2 (US), and TiO_2 (MW) are represented in Fig. 2. The particles size of TiO_2 was spherical shape and monodispersion. It is clearly observed that particle size of TiO_2 that was treated with microwave radiation (0.4 μm) was smaller than other TiO_2. The particle size of TiO_2 (SG) (3.0 μm) is larger than that of TiO_2 (US) (2.2 μm) (see Table 1).

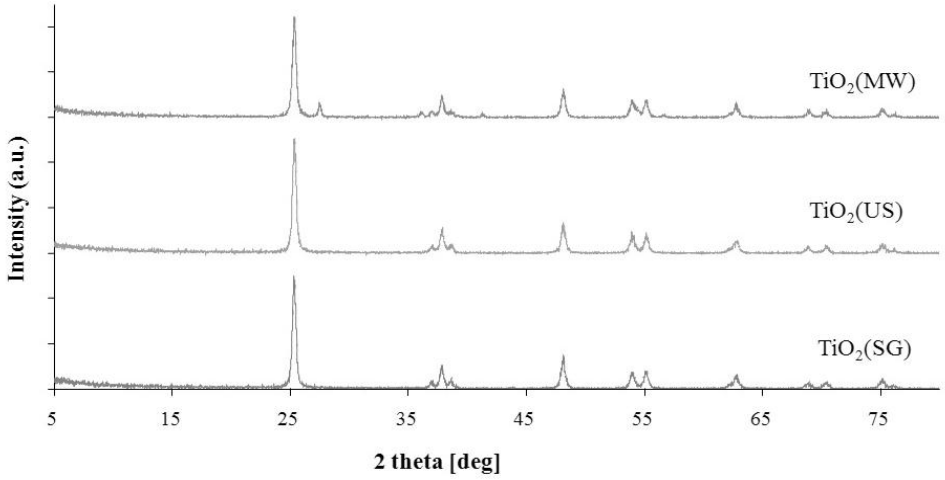

Fig. 1: X-ray diffraction patterns of TiO_2 (SG), TiO_2 (US), and TiO_2 (MW).

Table 1: Summary of XRD characterizations of the synthesized TiO_2.

Photocatalyst	Crystal phase[a] (%)	Crystallite size(nm)	Particle size (μm)
TiO_2 (SG)	A(100)	25.1	3.0
TiO_2 (US)	A(100)	25.1	2.2
TiO_2 (MW)	A(86)/R(14)	28.7/65.2	0.4

[a] A and R denote anatase and rutile, respectively.

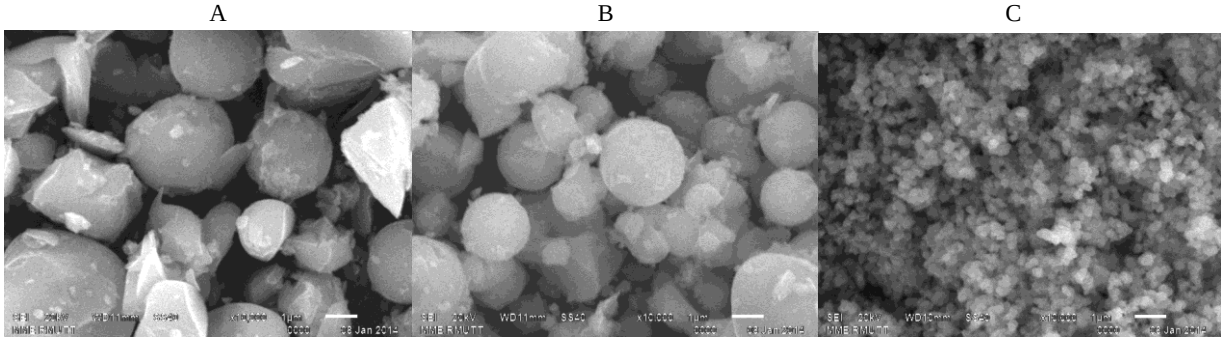

Fig. 2: SEM images (10000x) of TiO_2(SG) (A), TiO_2(US) (B), and TiO_2(MW) (C).

3.2. Photocatalytic reactions

The photocatalytic conversion of glucose is showed in Fig. 3. The photocatalytic conversion of glucose increased with long irradiation time. It also indicated that TiO_2 (MW) shows higher conversion of glucose (67.7%) than TiO_2 (SG) and TiO_2 (US) at 120 min. It could be implied that smaller particles of TiO_2 and well dispersion of particles of TiO_2 (MW) led the larger photoactive area. Therefore, its photocatalytic conversion was high.

The organic acid products were obtained from photocatalytic oxidation of glucose with synthesized TiO_2 is shown in term of pH (see Fig. 4). It was indicated that the increasing irradiation time influenced to the reduction of pH. The pH value of product solution of TiO_2 (MW) is lower than TiO_2 (SG) and TiO_2 (US). These results also correspond to the photocatalytic conversion of glucose. Interestingly, pH value of products solution of TiO_2 (MW) was lowest at 15 min (pH=2.5) after that it trended to increase. This phenomenon was explained that some organic acid products might be converted to CO_2 and H_2O via mineralization [13].

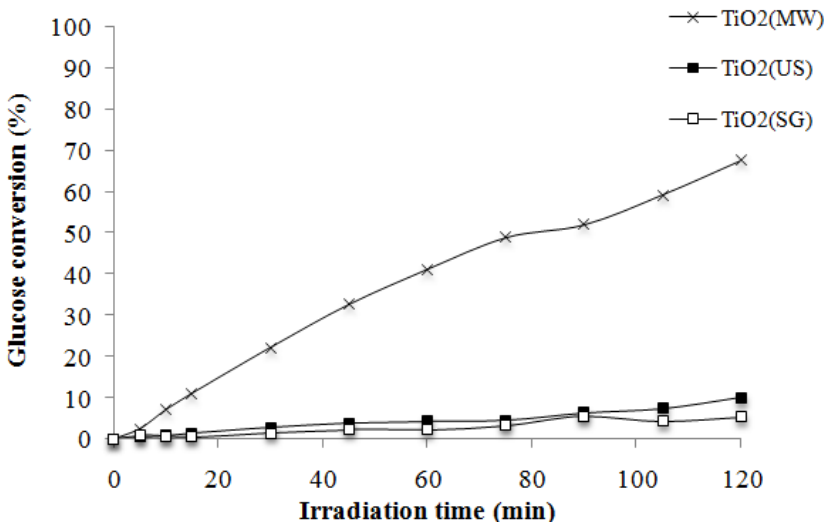

Fig. 3: Photocatalytic conversions of 1g/L of glucose in 10/90(v/v) water and acetronitrile with TiO_2 (various modified synthesis technique) for 120 min irradiation time.

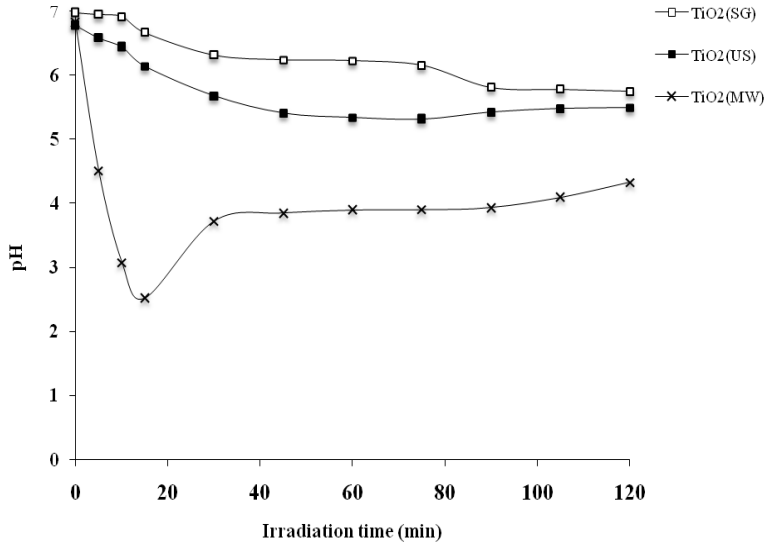

Fig. 4: Effect of modified technique of TiO_2 synthesis on pH of product solution in 120 min of irradiation time.

4. Conclusion

The synthesized TiO_2 was obtained from different modification techniques of sol-gel methods. These particles are in spherical shape. Experiments on TiO_2 (MW) showed the largest crystalline size of anatase crystal, but its particle size is smallest. It also showed mixture phase of anatase and rutile due to transformation of anatase to rutile phase by heat from the microwave irradiation. The small particles of photocatalysts affect high photocatalytic conversion of glucose to organic acids because high surface area of glucose adsorption site.

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