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Conversion of Lignin via Photocatalysis Using Synthesized Ag-TiO_2 Photocatalysts Sintered under Different Atmospheres

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Abstract: TiO_2 synthesized from sol-microwave method were modified by Ag loading by wetness impregnation technique. Sintering atmosphere during the photocatalyst preparation was adjusted by change of gases. In order to compare with Ag-TiO_2 calcined under air condition (conventional condition), Ag-TiO_2 was sintered under an inert (N_2) atmosphere (instead of air) and Ag-TiO_2 reduced in H_2 atmospheres (sintering 2 times) were prepared. Morphology and physical properties of Ag-TiO_2 were investigated by field-emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD). It was found that metal loading and sintering conditions did not affect agglomeration morphologies. Ag-TiO_2 photocatalysts sintered under N_2 atmospheres or ones reduced under H_2 could absorb more light as shown in gray or dark color. With 1%wt Ag loading on TiO_2, Ag peaks could not be found in XRD patterns. Anyway, Ag existing could be confirmed by EDS in FESEM images. Ag contents in Ag-TiO_2 sintered under N_2 or reduced in H_2 gas were found to be higher compared with one calcined in air. This implied that in Ag-TiO_2 sintered under N_2 or reduced in H_2 gasses, Ag^0 phase was greater formed compared with Ag^+ phase. Photocatalytic activity of synthesized TiO_2 was studied in order to apply in conversion of a waste from lignocellulosic biomass utilizations, i.e. lignin. In order to determine photocatalytic activity, lignin conversions were carried out with Ag-TiO_2 samples under UV-A irradiation for 5 h. The results showed that photocatalytic activities of TiO_2 could be improved by Ag loading. However, in term of sintering atmosphere, sintering under inert (N_2) atmosphere and re-sintering (reduced form) provided poorer photocatalytic activity than conventional calcination under air condition. This indicated that Ag^+ phase played an important role in Ag-TiO_2 activity of lignin conversion under UV irradiation.

Keywords: Photocatalyst, Lignin conversion, TiO_2, Silver loading, Sintering.

1. Introduction

Nowadays, environmental problems and inadequate energy have been seriously concerned, therefore alternative resources, especially, biomass has received much attention to utilize instead of non-renewable resources (e.g. fossil fuel, coal, and natural gas). Biomass is an attractive resources because it has many advantages such as low cost, renewable resources, and clean resources. Moreover, Thailand as an agricultural country can produce a lot of biomass resources (sugarcane, bagasse, corn, rice husk, rice straw, and others). Lignocellulosic biomass components (i.e. cellulose, hemicellulose, and lignin [1]) were used in different purposes (energy and chemical productions [2–4]). In lignocellulose utilizations, cellulose and hemicellulose are separated to be used, while lignin is left as a waste. Therefore, lignin can be derived from many processes such as paper or pulp processes, wood extractions, biomass ethanol productions, and biodiesel pretreatments [5]. Many processes, for instance, alkali pyrolysis [6], hydrothermal conversion [7], and electrochemical depolymerization [8] have been improved in order to manipulate lignin. Most of the lignin conversion processes have high energy consumption and harsh condition. Photocatalysis which enhances rates of several chemical reactions by light and catalyst was adopted in many applications, for instance wastewater purification, toxic chemical degradation, and also lignin degradation owning to low energy consumption and clean process [9].

TiO_2, semiconductor photocatalyst, has been used for many decades due to good stability, high activity, and low cost [10]. Wide energy band gap (~3.2 eV) [11] of TiO_2 limited electron excitation in UV, which contain less than 5% in solar energy spectrum [12]. Many techniques have been improved to solve the limitations of TiO_2 photocatalysts (metal, non-metal, and noble metal loading). Loading noble metal in TiO_2 such as Ag, Au, and Pt was reported to shift light absorption ability from UV to visible region and reduce electron and hole recombination [13-16]. Ag-TiO_2 photocatalysts have been applied in various applications of photocatalysis, for example hydrogen (H_2) production from water via Ag-TiO_2 nanorods under visible light irradiation [17] and methylene blue degradation with synthesized Ag-TiO_2 photocatalysts under visible light irradiation [18].

In photocatalytic conversion of lignin, many efforts focused on determining the suitable conditions for lignin conversions, such as type photocatalyst, pH condition, temperature, lignin concentration, and photocatalyst loading [5,19–21]. Only few researches focused on Ag-TiO_2 and no research studied effects of Ag forms in Ag-TiO_2 via change of sintering conditions on lignin conversion. In this research, TiO_2 were synthesized (by sol-microwave method) and modified by Ag (by wetness impregnation method). The Ag-TiO_2 photocatalysts were sintered under different conditions to provide different forms of Ag. The effects of sintering conditions on morphologies, properties, and photocatalytic activities of photocatalysts on lignin conversion process were investigated.

2. Experimental

2.1 Materials

Titanium (IV) butoxide ($Ti(OC_2H_9)_4$, Sigma Aldrich), acethylacetone ($CH_3CH_2COCH_2CH_3$, Sigma Aldrich), and isopropyl alcohol (C_3H_7OH, RCI Labscan) were used to prepare titanium dioxide (TiO_2). TiO_2 was modified using silver nitrate ($AgNO_3$, RCI Labscan). Kraft lignin (alkali type, Sigma Aldrich) was purchased to use in the reaction. Deionized water (DI) was used throughout an experiment.

2.2 TiO_2 synthesis

TiO_2 was synthesized by sol-microwave method as follows. Titanium (IV) butoxide ($Ti(OC_2H_9)_4$) as a precursor were mixed under stirring for a few min with acethylacetone ($CH_3CH_2COCH_2CH_3$) which is used to control the hydrolysis and condensation reaction. Isopropyl alcohol (C_3H_7OH) and deionized water were slowly dropped into the mixture under magnetic stirring, respectively. The molar ratio of TiBu:i-PrOH:ACA:H_2O was 0.032:0.784:0.032:4.444. The mixture was stirred for 10 min and then was brought to a microwave oven (Whirlpool, 2.45 GHz, 970W) for 4 min. Subsequently, the solution was dried in an oven at 80 °C overnight. The photocatalysts were then calcined at 500 ºC for 2 h to remove residual carbons and impurities, and to obtain crystal phases.

2.3 Modifications of TiO_2

Ag loading on TiO_2 (Ag-TiO_2) was prepared with 1 wt. % Ag via wetness impregnation method. $AgNO_3$ was dissolved in DI water and then slowly dropped into synthesized TiO_2. Obtain photocatalysts were dried in an oven at 80°C overnight. After that, photocatalysts were calcined under air in a muffle furnace (Chavachote Co.) while sintering under inert gas (N_2) in a tube furnace (Carbolite STF 15/180) at 400°C for 3 h. Sintering under H_2 was processed in a tube furnace (Carbolite STF15/180) at 400°C for 3 h after air calcination. In this work, photocatalysts were named shortly, for example 1Ag-TiO_2 (Air)" represents "1%-wt-Ag loading on TiO_2 which was calcined under air condition".

2.4 Characterizations

Field-emission scanning electron microscopy (FESEM; Hitachi SU-6600) with energy dispersive spectroscopy (EDS) were performed in order to obtain morphologies and elemental compositions on photocatalyst surface. Crystal phase compositions were determined by X-ray diffraction (XRD; Bruker D-76181 Karlsruhe) with Cu-Kα radiation (λ=0.15418 nm). The crystallite sizes were calculated using Scherrer equation (Equation (1)):

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{1}$$

where D is an average crystallite size, K is a coefficient (0.94), λ is an X-ray wavelength, β is the full width at half the maximum (FWHM) in radians, and θ is the Bragg angle.

2.5 Photocatalytic conversion of lignin

Acetonitrile (ACN) and DI water were mixed in the volume ratio of 80:20 v/v and used as the solvents of lignin. Kraft lignin was dissolved in the solvent in concentration 1,000 mg/L. The lignin solution and Ag-TiO_2 photocatalysts were mixed and transferred into a Pyrex cylindrical double-walled reactor which is located in wood box has mercury lamp as light source (UV 400 W, λ_{max} 365 nm) located beside the reactor. The reaction was processed at first 30 min under dark to homogenize solution. After 30 min, the light was turned on to start photocatalytic conversion of lignin. The mixture of photocatalyst and lignin was continuously stirred during experiment. In order to control reaction temperature, water cooler was circulated during process. The solution was sampled from reactor after reaction (5 h) to analyze. The samples from reaction were filtrated by a 0.45-µm PTFE syringe filter to remove catalyst before analysis by UV-vis spectroscopy. Lignin conversions were monitored by UV-vis spectroscopy via absorbance values at the wavelength of 280 nm which is originated from phenolic hydroxyl group and aromatic ring of lignin [5] using Equation (2):

$$Conversion(\%) = \frac{C_o - C_t}{C_o} x100 \tag{2}$$

where C_0 is an initial lignin concentration and C_t is a concentration of lignin at the sampling time of t.

3. Results and Discussion

In term of photocatalyst appearances, synthesized TiO_2, Ag-TiO_2 photocatalysts calcined under conventional condition (air) [so called Ag-TiO_2 (air)], Ag-TiO_2 sintered under an inert gas (N_2) [so called Ag-TiO_2 (N_2)], and Ag-TiO_2 reduced under H_2 [so called Ag-TiO_2 (H_2)] were white, gray, dark gray, and black, respectively, as shown in Figure 1. Color appearance of Ag-TiO_2 (air) in gray was same with previous study [22]. The results can be implied that light absorption abilities of TiO_2 were increased with Ag loading. Black color in Ag-TiO_2 (H_2) distinctively shows potential to absorb all visible light spectrum.

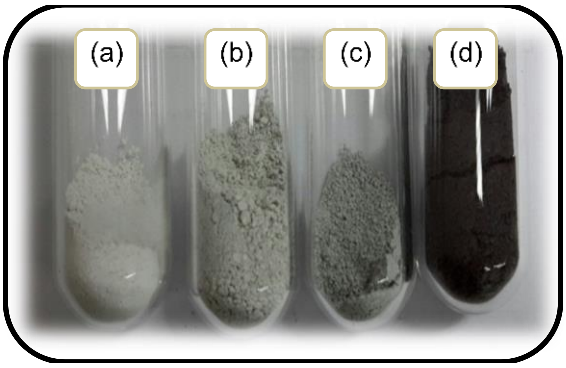

Figure 1. Micrographs of photocatalysts sintered at different atmospheres: (a) TiO_2, (b) 1Ag-TiO_2 (Air), (c) 1Ag-TiO_2 (N_2), and (d) 1Ag-TiO_2 (H_2).

FESEM was performed in order to observe the different agglomeration morphologies of TiO_2 and Ag-TiO_2 (Figure 2). Low agglomerations of particles are found in synthesized TiO_2 which may happen during sintering. Ag loading via impregnation technique and sintering under different atmospheres cannot significantly affect particle agglomeration in Ag-TiO_2 photocatalysts as shown in the figure.

Table 1. Elemental compositions of photocatalysts investigated by EDS.

Photocatalyst	Mass Composition (%)		
	Ti	O	Ag
TiO_2	45.64	54.36	-
1Ag-TiO_2 (Air)	66.69	32.17	0.87
1Ag-TiO_2 (N_2)	90.88	6.76	2.36
1Ag-TiO_2 (H_2)	70.62	27.72	1.66

EDS was conducted to confirm existing Ti, O, and Ag elements as shown in Table 1. Elemental distributions of Ag-TiO_2 are shown in Figure 3. It was found that Ag did not well distribution on all TiO_2 photocatalyst surfaces as related with some agglomerations in the FESEM images. TiO_2 shows only Ti and O elements, while in Ag-TiO_2, Ag contents are in the range of 0.87-2.36 wt.% (even though the desired loading was 1 wt.%). The lowest Ag content and the highest O compositions were found in 1Ag-TiO_2 (Air) compared with other Ag-TiO_2 samples, because of rich oxygen environment during the conventional calcination. Sintering under inert gas (N_2) and re-sintering under H_2 could reduce silver oxide to Ag, resulting in increase in Ag composition and decrease in O composition, compared with 1Ag-TiO_2 (Air).

TiO_2 and Ag-TiO_2 photocatalysts sintered under different atmospheres were characterized by XRD to evaluate crystallite phases as shown in Figure 4 and Table 2. Both synthesized TiO_2 and Ag-TiO_2 photocatalysts show peaks of anatase (JCPDS NO.21-1272) and rutile (JCPDS NO.21-1276) phases with major of anatase phase (>80%). Major peaks at 38.4° and 44.5° represented Ag^0 nanocrystalline peaks cannot be appeared on XRD pattern in all Ag-TiO_2 photocatalysts. Moreover, peak of Ag_2O (major peaks at 32.8° and 38°, JCPDS NO. 41-1104) is not also found from the XRD patterns in all Ag-TiO_2. This may be because of low contents or small crystallite sizes of Ag on TiO_2 as stated in previous work [19,20] which there is no Ag peaks even in 5 %wt Ag loading. However, Ag contents in Ag-TiO_2 were previously confirmed by EDS.

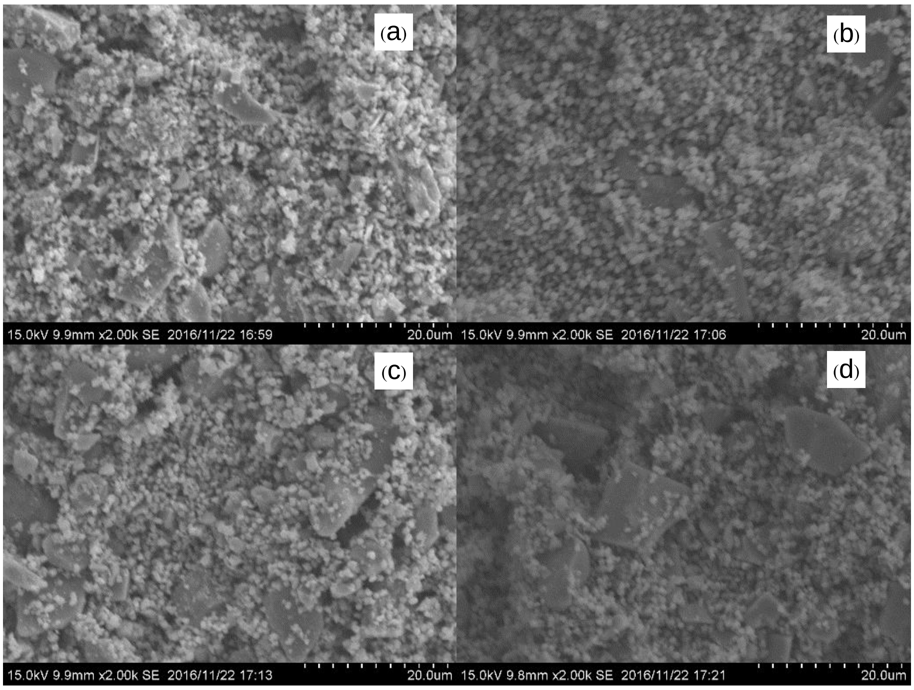

Figure 2. SEM images of photocatalysts sintered at different atmospheres: (a) TiO_2, (b) 1Ag-TiO_2 (Air), (c) 1Ag-TiO_2 (N_2), and (d) 1Ag-TiO_2 (H_2).

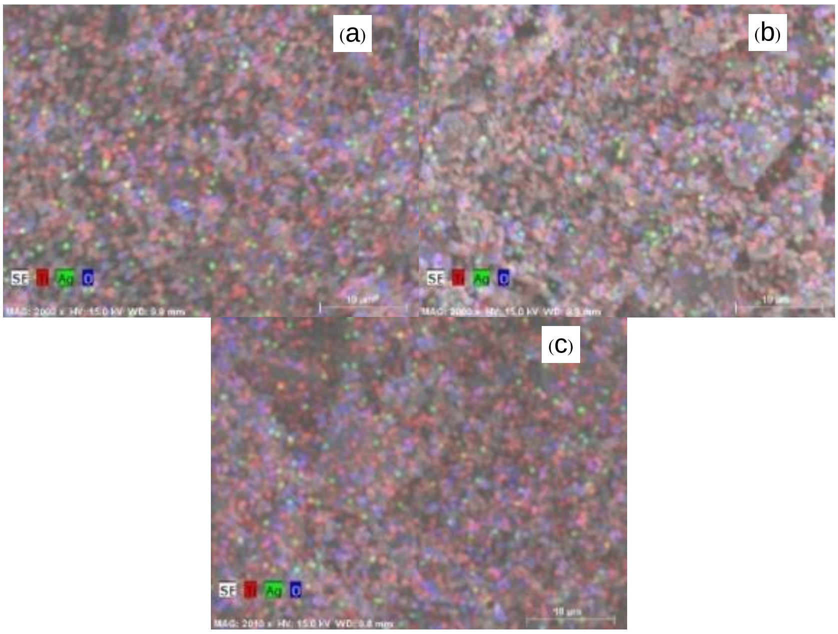

Figure 3. Elemental mapping of (a) 1Ag-TiO_2 (Air), (b) 1Ag-TiO_2 (N_2), and (c) 1Ag-TiO_2 (H_2).

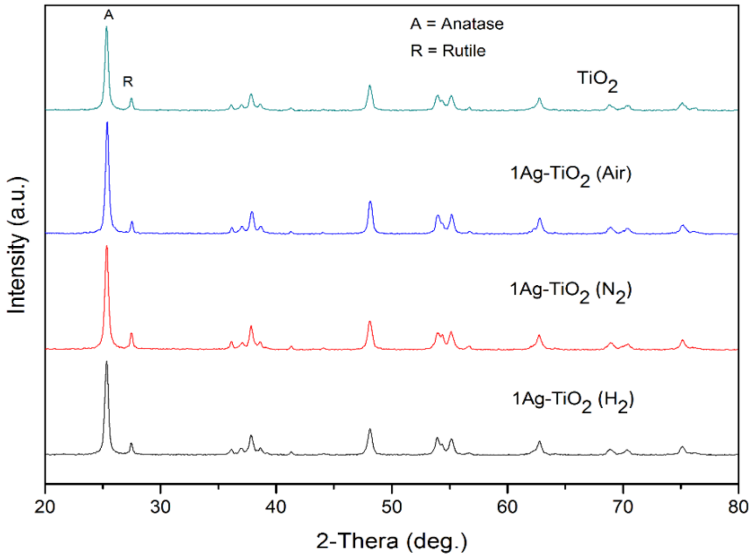

Figure 4. XRD patterns of synthesized TiO_2 and Ag-TiO_2 sintered under different atmospheres.

Table 2. Crystallite sizes and phase contents of synthesized TiO_2 and Ag-TiO_2 sintered under different atmospheres.

Photocatalyst	Phase (%)		Crystallite Size (nm)	
	Anatase	Rutile	Anatase	Rutile
TiO_2	86.73	13.27	24.35	33.45
1Ag-TiO_2 (Air)	90.66	9.34	25.01	35.58
1Ag-TiO_2 (N_2)	85.96	14.04	22.88	32.41
1Ag-TiO_2 (H_2)	88.20	11.80	22.33	34.13

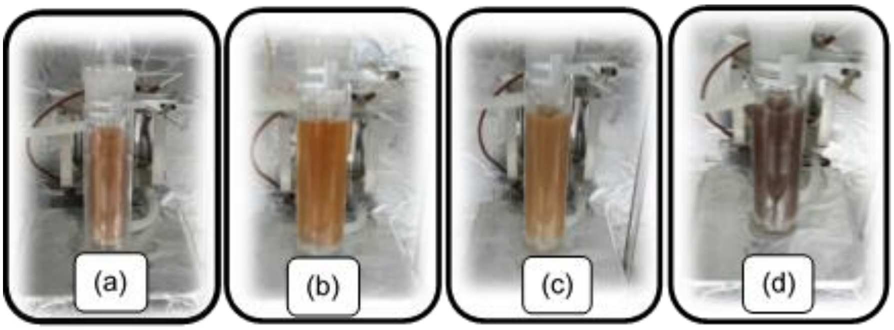

Figure 5. Lignin solutions before UV irradiation; (a) TiO_2 (b) 1Ag-TiO_2 (Air) (c) 1Ag-TiO_2 (N_2) (d) 1Ag-TiO_2 (H_2).

After photocatalyst preparation, effects of Ag loading and sintering conditions (air, N_2, and H_2) of photocatalysts on lignin conversion were further determined. Kraft lignin and ACN/H_2O were dissolved and mixed with photocatalysts sintered different atmospheres (Figure 5) loading of 1,000 mg/L. Batch reactions were conducted under UV irradiation for 5 h as shown in Figure 5. Lignin conversions are shown in Table 3.

Synthesized TiO_2 shows the lowest lignin conversion compared with synthesized TiO_2 loaded with 1% wt Ag (Ag-TiO_2). The results can be indicated that 1% wt of Ag could improve activity of TiO_2 photocatalyst in lignin conversion. Sintering under different conditions had effects on lignin conversion. The highest lignin conversion was found in Ag-TiO_2 (Air) which has high Ag^+ phase in TiO_2 (Air). Reducing Ag-TiO_2 under H_2 atmosphere (high Ag^0 content) provided the lowest lignin conversion. The colors of solution (dark) of Ag-TiO_2 (H_2) may affect to light available for electron excitation in photocatalysis. Although, the mechanism of lignin conversion via photocatalysis did not be confirmed in this work, the proposed mechanism had been currently reported in a previous research [21]. The high active species from photocatalysis (OH•, H•, and •O_2) lead to cleavage β-O-4 lignin linkages. Therefore, Ag^+ and Ag^0 phases on TiO_2 played an important role to provide high active species and improve photocatalytic activity in lignin conversion.

Table 3. Lignin conversions (lignin concentration = 1 g/L, catalyst = 1g/L, UV 400 W, λ_{max} 365 nm, 5h).

Photocatalyst	Conversion (%)
TiO_2	16.23
1Ag-TiO_2 (Air)	33.82
1Ag-TiO_2 (N_2)	27.66
1Ag-TiO_2 (H_2)	24.52

4. Conclusion

Synthesized TiO_2 was modified by Ag and sintered under different atmospheres. The results showed that Ag loading and sintering conditions did not affect agglomeration morphologies. Ag-TiO_2 photocatalysts sintered under N_2 atmospheres and under H_2 could absorb more light as shown in gray and dark colors, respectively. Ag peaks of 1%wt Ag-TiO_2 could be found on XRD patterns. However, EDS in FESEM images can confirmed Ag existing. Ag contents in Ag-TiO_2 sintered under N_2 or reduced in H_2 gas were higher than one calcined in air. This implied that in Ag-TiO_2 sintered under N_2 or reduced in H_2 gasses, Ag^0 phase was greater formed compared with Ag^+ phase. In lignin conversion, TiO_2 activities could be improved by Ag loading. However, in term of sintering atmosphere, re-sintering (reduced form) provided poorer photocatalytic activity than conventional sintered ones even in ones sintered under inert (N_2). This indicated that Ag phases played an important role in Ag-TiO_2 activity on lignin conversion under UV irradiation. Ag phases in Ag-TiO_2 in both conditions (N_2 and H_2) provided lower photocatalyst activity than Ag_2O phases.

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