Silver Doped Titania Materials on Clay Support for Enhanced Visible Light Photocatalysis

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This paper presents a study on the development of silver doped titania materials on clay support and their application for phenol photooxidation. Silver was incorporated by direct calcination of the sol-gel titania with silver nitrate added in various amounts. The silver ion was reduced during calcination of the sol-gel material via decomposition of silver nitrate. The structural characters of materials were studied by X-ray diffraction (XRD), diffuse reflectance spectra (DRS). The photocatalytic activity of silver doped titania photocatalyst and that of this mixture on clay support for phenol degradation were examined. The addition of increasing amounts of silver, for batches of samples, significantly increases the rate of degradation of phenol. This is attributed to the increasing visible absorption capacity due to the presence of silver nanoparticles. The better separation between electrons and holes on the modified TiO$_2$ surface allowed more efficiency for the oxidation reactions.

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I. INTRODUCTION

In recent years, because of industrialization, a large amount of organic substances has been filled in environment. Many of them are toxic and nonbiodegradable. Consequently, there is a need for treatment of persistent organic compounds.

Titanium dioxide illustrates such type of promising materials used in waste water treatment. For instance, TiO$_2$ is able to induce advanced oxidation processes under illumination in which organic pollutants can be completely mineralized to CO$_2$ and H$_2$O [1]. TiO$_2$ exhibits high photoelectrochemical stability. Indeed, their energy band positions are well matched to produce both O$_2$*• and OH* radicals, from dissolved oxygen and water molecules, respectively [2]. However, it has a band gap of 3.2 eV and suffers as a consequence of low solar to chemical conversion efficiencies which do not exceed 1% [3]. Moreover, titanium dioxide has photocatalytic effects only when exposure to UV light.

To overcome these disadvantages, attention has been paid to metal ions doped titania, which can extend the photosresponse of TiO$_2$ based materials to the visible region. Their high efficiencies proved that it can replace pure TiO$_2$ and enhance the photocatalytic conversion. Ho et al. [4] synthesized a catalyst by doping sulfur atoms into the lattice of anatase TiO$_2$ that can efficiently degrade 4-chlorophenol under visible light irradiation. The photocatalytic oxidation of toluene in gas phase over N-doped TiO$_2$ powders was studied [5] and it was found that more than 80% of toluene was mineralized to CO$_2$ and H$_2$O under visible light irradiation. In another work [6], researchers developed a simple method to prepare highly visible-active nanocrystalline N-doped TiO$_2$ photocatalysts by calcination the hydrolysis product of tetraethyl titanate with ammonia solution and found that the absorption spectrum of TiO$_2$ shifted to a lower energy (higher wavelength) region.

Developing novel catalyst materials that are active under sunlight irradiation is a new approach in recent years. One interesting achievement is the use of silver doped titania materials. Silver can trap the excited electrons from TiO$_2$ and leave the holes for the degradation reaction of organic species [7, 8]. It also results in the extension of their wavelength response towards the visible region [9, 10]. Moreover, silver particles can facilitate the electron excitation by creating a local electric field [11], and plasmon resonance effect in metallic silver particles shows a reasonable enhancement in this electric field [12]. The effect of Ag doping on titania and its photocatalytic activity by UV irradiation was studied by Chao et al. [13], and they found that Ag doping promotes the anatase to rutile transformation, which is attributed to the increase in specific surface area which results in the improvement in photocatalytic activity, and enhances the electron-hole pair separation.

In addition, it is easier to collect catalyst if it is immobilized on support; therefore, there is no secondary pollution. Bentonite support is widely known for its availability and cheapness; therefore its applicability in Vietnam is promising.

In this paper the influence of the amount of silver doping on TiO$_2$ on clay support and calcination temperature on the photocatalytic activity of the materials are presented; and the role of surface area, surface texture,
and band gap energy on photocatalytic oxidation of phenolics explored. Moreover, the removal of phenol was investigated to evaluate the relative photocatalytic activity of the prepared photocatalyst samples.

II. EXPERIMENTAL

A. Materials

Thanh Hoa bentonite provided by Truong Thinh company, titanium tetraisopropoxide (97%), acetic acid (99.7%) and silver nitrate (99%) were purchased from Merk. Phenol was of analytical reagent grade and used without further purification.

B. Catalyst preparation

The samples were prepared by a modified sol-gel route [14]. 12 mL titanium isopropoxide was added to 23 mL acetic acid with continuous stirring. After that, 72 mL water was added to the mixture drop by drop with vigorous stirring. The solution was kept stirring for 6 h until achieving a clear transparent sol. Dried at 100°C, after that it was calcined at 600°C for 2 h at a ramp rate of 5°C/min. To prepare silver doped titania on clay support, the above procedure was used, but instead of adding water, we added 72 mL silver nitrate solutions (1, 2.5, 5, 7.5 and 10 % wt) to the mixture of titanium isopropoxide and acetic acid. After that, the mixture was dropped in clay suspension. The dried powders were calcined at different temperature (500, 600, 700 and 800°C) for 2 h at a ramp rate of 5°C/min. The photocatalytic activities of the materials were studied by examining the degradation reaction.

D. Catalytic characterization

Catalytic characterization was investigated by X-ray diffraction method using D8 ADVANCE instrument (Bruker-Germany), Diffuse reflectance spectroscopy (UV-VIS- Jasco V-650-Spectrometer -Japan). Concentration of phenol was determined by spectrophotometric method using UV- VIS Novaspec II instrument (Germany) with 4-amino antipyrine as color agent at 510 nm. The mass fraction of rutile in the calcined samples was calculated by Spurr formula (Eq. (1)) which is the relationship between integrated intensities of anatase (101) and rutile (110) peaks, where \( I_A \) and \( I_R \) are the integrated peak intensities of anatase and rutile peaks, respectively.

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X_R = \frac{1}{1 + 0.8 \frac{I_A}{I_R}}
\]  

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Figure 1 shows the effect of calcination temperature on the phase change of the Ag-doped titania. From these
two patterns, it is easy to see that there is no rutile form of titania when calcined at 600°C. But when increasing calcination temperature to 700°C, there is high peaks of rutile form (rutile form is more than 60% - using equation (1) to calculate). Other studies in this area have reported that the anatase to rutile transformation for silver doped titania without support can occur at temperatures lower than 700°C [15]. This obviously indicates that calcination temperature has effect on modification of titania.

This method provides well dispersed silver in samples calcined at 600°C, as the presence of Ag2O3 is only suspect in the Ag-TiO2 sample calcined at 700°C. It is an interesting point because formation of Ag (I) would be expected rather than Ag (III). Ag (III) is a strong oxidation agent; therefore Ag (III) can hardly be formed in catalyst.

XRD pattern of 2.5% wt Ag doped titania on clay support calcined at 700°C (Fig. 2 (a)) has no peaks of rutile. Figure 2(b) shows that increasing amount of Ag to 10% wt, there are still no peaks of rutile but only those of a unknown substance (can be Ag2O3) and anatase. It is noticeable because without support there are peaks of rutile at even lower calcination temperature. In different forms of titania, anatase form has the highest catalytic property. Therefore, beside its easiness to collect after use, having only anatase form when calcined at high temperature is one advantage of the catalyst.

B. UV/VIS diffuse reflectance spectra and band-gap energy

Diffuse reflectance spectroscopy (DRS) was used to record absorbance capacity of the powders. Figures 3 and 4 present UV/VIS absorption spectra of the prepared TiO2 samples doped with Ag. The intensity of this absorption bands depend on increasing silver content doped TiO2 on clay support. As a general trend, increasing amounts of Ag to a certain amount results in a higher visible absorbance capability of the materials.

The UV/VIS diffuse reflectance spectroscopy method was employed to estimate band-gap energies of the prepared catalyst. The maximum wavelength required to promote an electron depends upon the band-gap energy $E_{bg}$ of the photocatalyst. Band-gap energy is given by equation [16]:

$$E_g = \frac{1239.8}{\lambda (\text{eV})}$$

Where $\lambda$ is the wavelength in nanometers.

![FIG. 3: Absorption spectra of (a) 5% wt Ag - TiO2/Bent vs. undoped TiO2 and (b) Ag - TiO2/Bent with various percents of Ag (1) 1% wt, (2) 2.5% wt, (3) 5% wt (4) 7.5% wt and (5) 10% wt](http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/))

![FIG. 4: Catalytic property of (a) Ag - TiO2/Bent calcined at various temperatures and (b) Ag - TiO2/Bent with various percents of Ag](http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/))

C. Photocatalytic activity

Photoactivity experiments were conducted in 100 mg.L$^{-1}$ phenol solution under the irradiation of sunlight. Photodegradation rates, presented as phenol concentration remaining in solution, are shown in Fig. 4.

These results clearly demonstrate that the degradation rate increases with the percentage of Ag up to 2.5% . Further increase in Ag content in the catalyst leads to a slight decrease in degradation rate. It can be seen that
there exists a good correlation between the light absorption properties and the photocatalytic activity of the samples. When the Ag content is between 1% wt - 2.5% wt, doping can significantly improve the photocatalytic activity of TiO₂. But when the dopant concentration is more than 2.5% wt, the photocatalytic activity decreases, which means that more doping may convert the dopant from the trap center to the combination center of the electron and the hole [17], thereby resulting in a decrease in the photocatalytic ability of TiO₂.

IV. CONCLUSION

1. Silver doped titanium dioxide materials on clay support were successfully synthesized and different doping concentrations and calcination temperatures were analyzed. XRD patterns show that in silver doped TiO₂ on clay calcined at 700°C, titania exists in only anatase phase.

2. DRS shows that doping Ag can make the light spectrum of TiO₂ move toward the visible light and increase the ability of absorbing light.

3. The photocatalytic experiments indicate that there exists a favorite dopant content of 2.5% wt. More or less of the favorite content are both detrimental to the photocatalytic activity of TiO₂.

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