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The promoting role of bismuth for the enhanced photocatalytic oxidation of lignin on Pt-TiO_2 under solar light illumination

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ABSTRACT

In this work, bismuth (Bi) and platinum (Pt) were utilized to promote the oxidation of lignosulfonate over TiO_2 under solar light illumination at facile condition. The characterization results revealed the presence of Bi and Pt covering on TiO_2 surface with zero valent state. And, the Bi1%/Pt1%-TiO_2 photocatalyst performed excellent reactivity in oxidation of lignosulfonate to produce valuable compounds and CO_2 due to the generation of photo-generated hole (h^+) and superoxide radicals ($O_2^{\bullet}$), which were confirmed by quenching experiments. After 1 h of photocatalytic reaction, almost 85% of lignosulfonate was conversed into guaiacol, vanillic acid (VA), vanillin, 4-phenyl-1-buten-4-ol and other intermediates that were identified and quantified using HPLC. We found that the amount ratio of added Bi and Pt was the essential effect to the oxidative efficiency of lignin due to the produced additional active sites on TiO_2 surface. This study provides a new strategy for generating h^+ and $O_2^{\bullet -}$ radicals under solar light and suggests its application for the selective oxidation of lignin.

1. Introduction

With the increasing concerns over the long term effects of global climate change and depletion of fossil fuels, there has been a growing interest to use lignocellulosic biomass for the production of chemicals and fuels [1,2]. However, sustainable operation of lignocellulosic bio-refineries is pending on the development of cost effective and robust integrated processes that fully utilize cellulose, hemicellulose and lignin.

As a natural aromatic biopolymer, lignin provides a unique opportunity for the production of aromatic chemicals and fuels. Accordingly, there has been a surge of interest in exploring new ways to convert lignin; that constitutes about 15%-35% of lignocellulosic biomass, to value-added products [3]. Among those valuable products, vanillin and vanillic acid are widely utilized as a flavoring or functional ingredient in food and cosmetic products [4,5]. Guaiacol is also used as an important raw material in production of medical compounds, dyestuff synthesis and bio-oil industry [6–8].

Gasification, pyrolysis, oxidation, hydro-processing, acid or based catalyzed de-polymerization, and liquid phase reforming, are some of various processes that has been reported in the literature for lignin conversion [9].

Considering the existing processes for lignin valorization, selective catalytic processes for the transformation of lignin at low-temperature and facile condition is expected to offer a significant economic advantage. Low temperature photocatalytic oxidation of lignin under ultraviolet (UV) illumination and the role of reactive specials, such as $^{\bullet}OH$, $O_2^{\bullet -}$, $^1O_2$ and photogenerated hole (h^+) radicals in this process have been investigated previously [10]. Photocatalytic transformation of lignin using hetero-nanostructured solar photocatalysts by combining semiconductors with noble metals, secondary semi-conductors, or by doping with metal or nonmetal atoms have been also examined [11–13]. Among those photocatalysts, noble metals-based materials, such as Pt/TiO_2 [14,15], Ag-AgCl/ZnO [16] and Pd/TiO_2 [17,18], have received growing attention for the selective oxidation of organic compounds.

Recently, a promising class of bismuth (Bi) promoted Pt- or Pd-based photocatalysts has been reported for the selective oxidation of chain alcohols or aromatic compounds [19–21]. The roles of bismuth in these catalysts have been suggested to be through one of several mechanisms including: (1) blocking of active sites through steric hindrance [22]; (2) generation of bismuth based alloy [23]; (3) protecting the noble metals from over oxidation [22]; (4) forming a new active center like Bi-OH_{ads} [24]; and (5) existing of soluble Bi species in reaction system [25,26].

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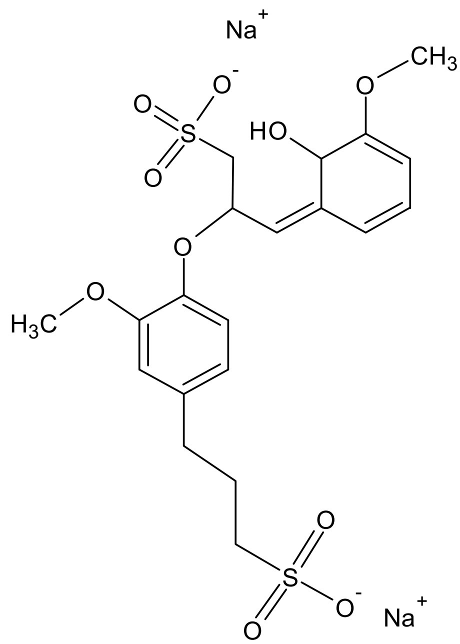

sodium of lignosulfonate

Fig 1. The molecular structure of sodium of lignosulfonate.

In this work, Bi and Pt co-modified TiO_2 was used for selective oxidation of lignin resulting in the generation of valuable compounds. The photocatalytic performance and structural properties of Bi/Pt-TiO_2 were estimated to understand the role of Bi and Pt in the photocatalytic process. A parallel study has also been carried out to confirm the dominant generated reactive oxygen species (ROS) from photocatalysts in photocatalytic process by degradation of methyl orange (MO) in the presence of several scavengers. These photocatalysts were characterized by X-ray diffusion (XRD) and X-ray photoelectron spectroscopy (XPS) before and after the oxidation of lignin.

2. Experimental

2.1. Materials and chemicals

Lignin (sodium of lignosulfonate, as shown in Fig. 1), titanium dioxide (P25), bismuth nitrate ($Bi(NO_3)_5{\cdot}5H_2O$), chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$), sodium borohydride ($NaBH_4$), sodium fluoride (NaF), 1,4-benzoquinone (BQ), triethanolamine (TEA), isopropanol (IPA), absolute ethanol, HCl and NaOH were purchased from by Sigma-Aldrich. All chemical reagents were of analytical grade and used without further purification. Ultrapure water (resistivity >18 MΩ·cm) obtained from a water purification system (Millipore, France) was used.

2.2. Characterizations

A Quanta 200 SEM was employed to characterize the morphology of the nanoparticles. The phase detection and analysis were performed by XRD (Rigaku Miniflex 600) using Cu *Kα* radiation. The XPS analysis was conducted on a Thermo Scientific K-Alpha.

2.3. Photocatalyst preparation

The synthesis of Pt/Bi-TiO_2 was performed by using a reduction method. In brief, 1 g of P25 and the designed amount of $BiNO_3{\cdot}5H_2O$ (1%, atomic ratio of Bi to Ti) and $H_2PtCl_6{\cdot}6H_2O$ (1%, atomic ration of Pt to Ti) were added together in 10 mL of water. The mixture was stirring for 15 min and then 5 mL of $NaBH_4$ solution (1 M) was added dropwise into the mixture. After a continuous stir for another 15 min, the obtained gray powder was washed with ethanol and water, and then dried at 80 °C under H_2 atmosphere for 2 h. The final obtained particle was Pt/Bi-TiO_2. To produce Pt-TiO_2 or Bi-TiO_2, we used the same method mentioned above without adding $Bi(NO_3)_3{\cdot}5H_2O$ or $H_2PtCl_6{\cdot}6H_2O$, respectively. All samples were kept in a vacuum storage to avoid oxidation until we used them.

2.4. Experimental procedure

The photocatalytic oxidation of lignin was conducted at room temperature. Catalyst (1 g/L) was added to 100 mL of a lignin (100 mg/L) solution in a 200-mL self-designed glass reactor with a quartz window. The suspension was equilibrated in the dark condition for 15 min prior to illumination. The photocatalytic activity of all as-prepared samples was evaluated under 300 W Xe lamp. The solar light intensity measured with a visible-light radiometer (Model: FZ-A, China), was 125 mW/cm^2. The photocatalytic reactions were monitored by sampling at designed time and filtered through a 0.22 μm PTFE filter to remove particles. Quenching experiments were performed similar to the degradation experiments except that radical scavengers, IPA (2 mM), NaF (2 mM), NaN_3 (2 mM), TEA (2 mM) and BQ (2 mM), were added to the reaction systems to investigate the contributory roles of reactive oxygen species (ROS) in the reactions. The pH values were adjusted by H_2SO_4 or NaOH. All batch experiments were done in duplicate. To analyze the stability of nanoparticles, the oxidation of lignin was repeated three times. After the first reaction, catalyst was washed with water twice and collected by centrifugation, then placed into fresh lignin solution for the next run.

The conversion of lignin, the yield of intermediates and the selectivity of those by-products were defined as follows:

$$\text{Conversion}(\%) = (C_0\text{-}C_{\text{lignin}}) \times 100/C_0$$

$$\text{Yield}(\%) = C_{\text{oxydate}} \times 100/C_0$$

Where C_0 is the initial concentration of lignin; C_{lignin} is the concentration of lignin at sampling time; and $C_{oxydate}$ is the concentration of the generated oxydate at given time, respectively.

2.5. Analytical methods

Samples were collected (0.5 mL for each sample) at given intervals using a 1 mL glass syringe and immediately filtered through

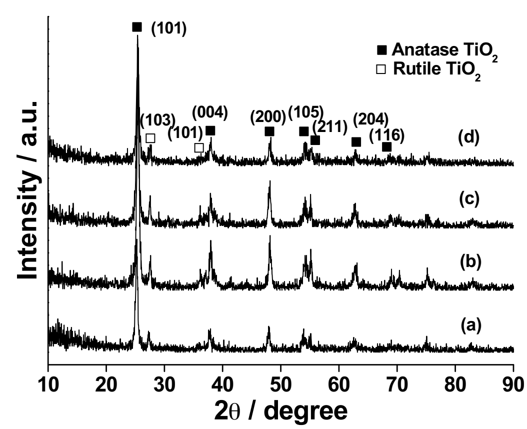

Fig. 2. XRD patterns of (a) TiO_2, (b) Bi1%-TiO_2, (c) Pt1%-TiO_2 and (d) Bi1%/Pt1%-TiO_2.