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CuO/WO_3 and Pt/WO_3 nanocatalysts for efficient pollutant degradation using visible light irradiation

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ABSTRACT

CuO/WO_3 and Pt/WO_3 nanocatalysts with a nanorod morphology were used for photodegradation of organic compounds using visible light irradiation. Both nanocatalysts were prepared using flame assisted spray pyrolysis method (FASP). The prepared nanocatalysts were mechanically stable during the agitation treatment for the photodegradation test due to good interconnection between WO_3 and co-catalysts. The enhancement of photocatalytic activity was observed after the addition of CuO and Pt as co-catalysts. The addition of CuO would change the morphology of WO_3 from nanorods to cubic. The optimal concentration of the CuO addition was 0.33 wt.%. A low Pt concentration (0.12 wt.%) was required for optimal photocatalytic activity of the Pt/WO_3 nanocomposite. The addition of Pt affected neither the morphology nor the crystallite structure of WO_3.

1. Introduction

Tungsten oxide (WO_3) is a visible-light-driven photocatalyst which has many potential applications: energy conversion devices [1–3], virus deactivation [4], and harmful pollutant degradation [5,6]. The optical band gap of WO_3 is approximately 2.7–2.8 eV, which allows it to absorb light that ranges from ultraviolet to blue ($\lambda < 455$ nm) [7,8]. In comparison to titania (band gap 3.0–3.2 eV) [7,9], WO_3 shows better photoabsorption in visible-light irradiation due to its smaller band gap. This ability opens the application of WO_3 for indoor pollutant treatment of volatile organic compound (VOC) gases using domestic light sources where ultraviolet light is limited. In outdoor applications, WO_3 has the potential to use sunlight as energy for the treatment of harmful pollutants in industrial waste-water, and has the potential for hydrogen production as well.

Bare WO_3 shows very low photocatalytic activity under visible light irradiation. Many attempts have been made to improve the photocatalytic activity of WO_3. The addition of a co-catalyst, such as platinum (Pt), gold (Au), and silver (Ag), enhances the photodegradation activity of WO_3 [5,6,10–12]. Thus far, Pt has been the most powerful co-catalyst for high-activity WO_3. Typically, electrons will be excited when a semiconductor catalyst is irradiated by light. Pt serves as a pool for electrons, thereby catalyzing the reduction of O_2 via a multi-electron route. As a result, an abundant amount of hydroxyl radicals ($OH^\bullet$) are available. These hydroxyl radicals ($OH^\bullet$) effectively degrade the target organic compounds. Thus, the effective excited electron consumption of multi-electron reduction results in an efficient charge separation and ensures high activity for Pt/WO_3. Unfortunately, the high cost of Pt is a primary impediment for a scale-up process.

To replace Pt as a co-catalyst, metal oxide and metal ion have been intensively investigated. Metal oxides of $CuBi_2O_4$ [13], $CaFe_2O_4$ [14], TiO_2 [15] and CuO [16,17] were prepared as a composite with WO_3. Also, the grafting of Cu [18] and Cu ion [19] onto the surface of WO_3 has been conducted. Among those methods, the utilization of CuO and $CuBi_2O_4$ as co-catalysts was most interesting. CuO and $CuBi_2O_4$ mix simply with WO_3 and create an efficient photocatalyst composite for volatile gas decomposition [13,16,17]. However, a problem occurs when photodegradation of organic components in aqueous solution is conducted. The composite of WO_3 and oxide co-catalysts disintegrates due to extensive stirring treatment during the photodegradation test. As a result, the co-catalyst effect is no longer observed. Therefore, an interconnected structure for co-catalyst-WO_3 composites that will be strong enough to resist mechanical treatment is highly desirable.

Herein, is shown the fabrication of CuO/WO_3 and Pt/WO_3 nanocatalysts using a flame assisted spray pyrolysis (FASP) method. This is a fast, continuous, and controlled method for the production of both nanoparticles and nanocomposites [8,20]. The prepared

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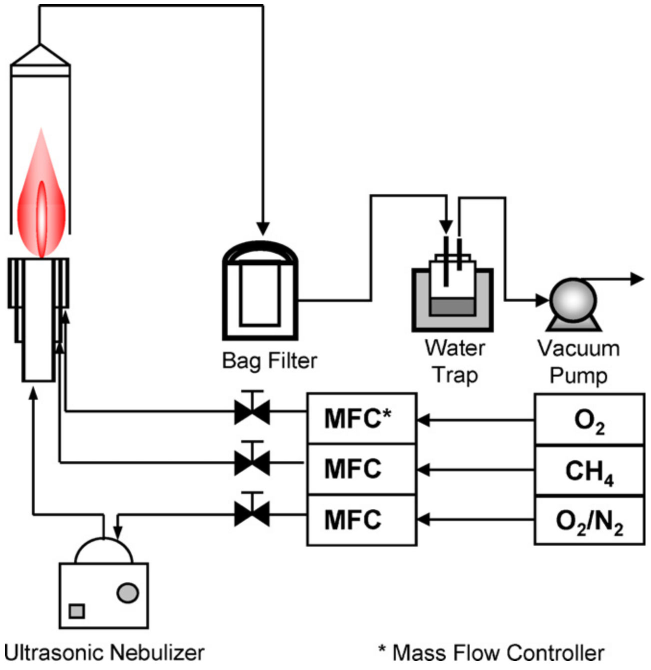

Fig. 1. Schematic diagram of flame assisted spray pyrolysis (FASP).

nanocatalysts have strong interconnection WO_3 and co-catalysts which were effective for organic compound degradation under visible light irradiation. In addition, the FASP method also was effective in the preparation of a Pt/WO_3 photocatalyst using a low Pt concentration. A low concentration of Pt is important in the practical application of a Pt/WO_3 photocatalyst.

2. Experimental

2.1. Preparation of CuO/WO_3 and Pt/WO_3 nanocomposites

The CuO/WO_3 and Pt/WO_3 nanocatalysts were prepared using FASP as shown in Fig. 1. FASP is comprised of three main parts: precursor atomizer, diffusion burner, and particle collector. The precursor was atomized using an ultrasonic nebulizer (NE-U17, OMRON, Japan) to produce droplets (average size 5 μm). The droplets were then transported to the flame zone using a carrier gas (O_2 or N_2). The prepared powder was collected using a bag filter and was used for further characterization. The preparation of both composites was carried out under optimal conditions. The CuO/WO_3 composite was prepared using a methane flow rate of 1 L/min (oxygen flow rate of 2.5 L/min) with an oxygen carrier gas flow rate of 2 L/min. In the case of Pt/WO_3, the flame was generated using a methane gas flow rate of 0.5 L/min (oxygen flow rate of 1.1 L/min) with a nitrogen carrier gas flow rate of 1 L/min.

The precursor chemicals were $5(NH_4)_2O{\cdot}12WO_3{\cdot}5H_2O$ (ammonium pentahydrate, 88–90%, Kanto Kagaku, Tokyo, Japan), $H_2PtCl_6{\cdot}6H_2O$ (98.5%, Kanto Kagaku, Tokyo, Japan), and CuO nanoparticles (11 nm, Nishin Engineering, Tokyo, Japan). The precursor was prepared by dilution of $5(NH_4)_2O{\cdot}12WO_3{\cdot}5H_2O$ with pure water with the concentration 0.01 M. The Pt and CuO were added to the solution with a calculated weight fraction that ranged from 0 to 0.5 wt.%. To facilitate better dispersion of CuO in the solution, homogenization was conducted using an ultrasonic cleaner for approximately 2 h. The prepared precursor was then used to prepare the nanocatalyst in the FASP method.

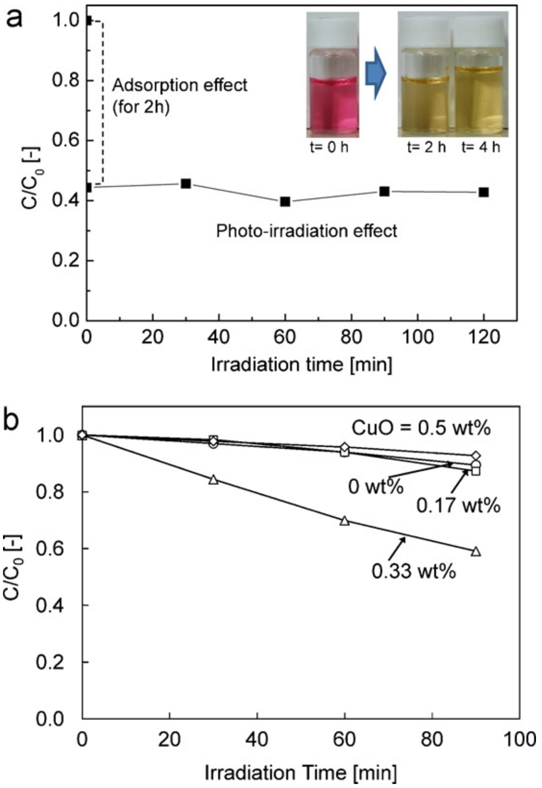

Fig. 2. Time–concentration chart of amaranth degradation using (a) CuO/WO_3 nanocomposite prepared by simple mixing of nanoparticles, the side reaction of organic compound oxidation produced Cu ions (inset) and (b) CuO/WO_3 nanocomposite prepared by FASP in different CuO concentrations.

2.2. Nanocatalysts characterization

The as-prepared nanocatalysts were characterized using field-emission scanning electron microscopy (FE-SEM), field-emission transmission electron microscopy (FE-TEM), X-ray diffractometer (XRD), Ultraviolet-visible Spectroscopy (UV–vis) and photoluminescence (PL). FE-SEM observations were carried out at 20 kV using an S-5000 (Hitachi Ltd., Tokyo, Japan). The characterization of the annealed powder was used to calculate particle size diameter. The calculation was conducted for about 1000 particles with the aid of Perfect Screen Ruler software. The crystalline nature of WO_3 was observed using TEM (JEM-3000F, JEOL, Tokyo, Japan) operated at 300 kV. The crystal structure of WO_3 was examined using an X-ray diffractometer (XRD, RINT 2200 V, Rigaku-Denki Corp., Tokyo, Japan). The XRD measurements were carried out using nickel-filtered Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA with a scan step of 0.02° and a scan speed of 4°/min. Photoabsorption characterization was conducted using a UV–vis spectrophotometer (UV 2450, Shimadzu, Kyoto, Japan). The PL measurement was conducted using a Shimadzu RF-5300PC. The PL intensity was measured at an excitation wavelength of 270 nm using a xenon lamp at a resolution of 0.2 nm. The PL graph give an information regarding the correlation between nanocatalysts composition and electron–hole recombination process.

2.3. Photodegradation test

To evaluate the photodegradation action of WO_3 nanocatalysts, amaranth ($C_{20}H_{11}N_2Na_3O_{10}S_3$, 90%, Sigma–Aldrich, Germany) was used. The amaranth ($C_{20}H_{11}N_2Na_3O_{10}S_3$) was chosen for the probe because it's resistance to self-degradation under light irradiation. The photocatalytic reaction was carried out in a pyrex glass