Applied Surface Science 362 (2016) 257–264

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis of Cu/TiO_2/organo-attapulgite fiber nanocomposite and its photocatalytic activity for degradation of acetone in air

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ARTICLE INFO

Article history:
Received 13 September 2015
Received in revised form
18 November 2015
Accepted 24 November 2015
Available online 2 December 2015

Keywords:
Attapulgite
Cu
TiO_2
Photocatalysis
Acetone

ABSTRACT

The Cu/TiO_2/organo-attapulgite fiber (CTOA) nanocomposite was synthesized by a facile method and was used for photocatalytic degradation of acetone in air under UV light irradiation. The as-prepared samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), transmission electron microscopy (TEM), UV–vis diffuse reflectance spectrum (UV–vis DRS), inductively coupled plasma (ICP) spectrometry and N_2 adsorption–desorption measurement. The results showed that the structure of organo-attapulgite (OAT) had no obvious change as compared to unmodified attapulgite (AT) and the attapulgite fibers in the OAT were well-dispersed. Both micropores and mesopores exist in the CTOA catalyst. The CTOA catalysts prepared at the Cu/TiO_2 molar ratio of 0.003 shows an excellent photocatalytic activity for the degradation of acetone in air. The synergistic effect of Cu species and cetyltrimethylammonium bromide modification can be responsible for the enhanced photocatalytic activity of the CTOA catalyst. The mechanism of the photocatalytic degradation of acetone by the CTOA catalyst was discussed.

1. Introduction

Volatile organic compounds (VOCs) are very important pollutants in air, which derived principally from combustion of fuel, transportation and decorative materials. VOCs have caused various environmental problems and serious harm to human health. So air pollution control has been paid more and more attention in recent years [1].

Semiconductor mediated heterogeneous photocatalysts (e.g. TiO_2, ZnO, SnO_2 and WO_3) have become a kind of popular materials that have great potential to control air pollutants. Titanium dioxide (TiO_2) as the most suitable semiconductor photocatalyst has been widely used for the degradation of VOCs because of its excellent chemical stability, strong oxidizing power and no secondary pollution characteristics [2–6]. VOCs always exist at low concentrations and spread rapidly in air. However, TiO_2 photocatalyst usually shows a weak adsorption of organic gases, which results in the low photocatalytic efficiency. Thus, efficient enrichment of VOCs by the catalysts is very important for improving the photocatalytic efficiency of TiO_2 photocatalysts. The organo-clay supported TiO_2 photocatalyst used in air pollution treatment have been studied in the past few years [7–9]. Attapulgite (AT), as the natural clay, shows high specific surface, surface charge characteristics and cation exchange ability. Previous studies have indicated that replacing inorganic cations of the AT with long-chain organic cations can increase the adsorption capacity of organic compounds [10–12]. Meanwhile, many studies have reported that the photocatalytic activity of TiO_2 catalyst could be improved by doping metal species effectively [13–15]. The doped metal species (e.g. Cu) could trap and subsequently transfer the photoexcited electrons on TiO_2 surface, which results in an increased rate of hydroxyl radicals ($OH^\bullet$) formation [14,16,17]. Some studies also indicated that dissolved metals increase the reaction rate via homogeneous pathway rather than a TiO_2 surface reaction [18]. However, there were few reports on the degradation of gaseous organic compounds in air by metal ion-doped TiO_2/organo-clay catalysts.

In this paper, an efficient Cu/TiO_2/organo-attapulgite fiber (CTOA) catalyst was designed and synthesized by a simple method. The photocatalytic activity of the CTOA catalyst was evaluated by degradation of acetone in air under UV light irradiation, which is a typical indoor air pollutant and can cause serious harm to nervous system and breathing system of humans. Effects of some preparation conditions (e.g. Cu content, mass ratio of CTAB/AT and treatment temperature) on the photocatalytic activity of the

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http://dx.doi.org/10.1016/j.apsusc.2015.11.218
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catalysts were studied. The mechanism for the photocatalytic degradation of acetone under UV light irradiation over the CTOA catalyst was also discussed.

2. Experimental

2.1. Materials

The attapulgite fiber used in this study was obtained from Xuyi, Jiangsu, China. Titanium tetrachloride ($TiCl_4$, SCRC, China), hydrochloric acid (HCl, SCRC, China), cetyltrimethylammonium bromide (CTAB, SCRC, China), cupric chloride ($CuCl_2 \cdot 2H_2O$, SCRC, China) and acetone (C_3H_6O, SCRC, China) were all of A.R. grade and were used without any further purification in the experiments. Deionized water was used in the whole study.

2.2. Preparation of organo-attapulgite (OAT)

Attapulgite (AT), a kind of hydrated magnesium aluminum silicate nonmetallic mineral, is a fibrillar silicate clay mineral with great hydrophilicity and low hydrophobicity [19]. In order to obtain a better compatibility with organic molecules, CTAB, which could exchange inorganic cations (e.g. Mg^{2+}, Ca^{2+}) of the AT, was used as the cationic surfactant to modify the AT.

The AT fiber was dispersed into deionized water with constant stirring to obtain a 0.4 wt% suspension. According to different mass ratios of CTAB/AT from 1/1 to 1/10, CTAB was added into the vigorously string suspension to obtain a mixture. During the process, the temperature was kept at 70 °C. Then the reaction mixture was stirred for 2 h and ultrasonically dispersed for 15 min. Then the mixture was washed by deionized water until no Br^- was detected by $AgNO_3$ aqueous solution (0.1 mol/L). The centrifugate was dried at 70 °C for 4 h to obtain the organo-attapulgite fiber (OAT).

2.3. Preparation of Cu/TiO_2/organo-attapulgite fiber (CTOA) catalysts

The Cu/TiO_2/organo-attapulgite fiber (CTOA) catalysts were prepared by a simple method. The $TiCl_4$ and $CuCl_2 \cdot 2H_2O$ were used as the precursors of TiO_2 and Cu species, respectively. A homogenized solution was prepared by adding dropwisely 4.4 mL $TiCl_4$ into 9.8 mL HCl aqueous solution (6 mol/L) under stirring at 25 °C until the molar ratio of HCl/$TiCl_4$ increased to 1.5. Then $CuCl_2 \cdot 2H_2O$ aqueous solution (0.12 mol/L) was added into the obtained homogenized solution under successive string at 25 °C to reach a Cu/Ti molar ratio of 0.003. After additional stirring for 30 min and aging for 6 h at room temperature, a Cu/TiO_2 sol was obtained.

The OAT fiber was dispersed in water by stirring for 2 h to obtain a 0.4 wt% OAT suspension. Then, the Cu/TiO_2 sol was dropwisely added into the suspension at 70 °C under a stirring speed of 650 r/min to reach a [Ti^{4+}]/AT ratio of 0.02 mol/g. The obtained mixture was stirred for additional 2 h and aged for 12 h at room temperature, and then was centrifuged and washed with deionized water until the pH of the filtrate was 2.0. Then the precipitate was dried in air at 70 °C (CTOA-70), and calcined at 300 °C (CTOA-300), 400 °C (CTOA-400) and 500 °C (CTOA-500) for 2 h, respectively.

For comparison, the TiO_2/attapulgite fiber (TAT) and the Cu/TiO_2/attapulgite fiber (CTA) catalysts were prepared using the AT as raw materials by the same procedure as described above. Pure TiO_2 was also prepared without adding any Cu species and attapulgite as described above.

2.4. Characterization

The structure and crystallinity of the as-prepared samples were characterized by X-ray diffraction (XRD) on an X-ray diffractometer (D/MAX-RB, Rigaku, Japan) with Cu Kα radiation at 40 kV and 100 mA in a scanning range of 2.5–70° (2θ). The chemical bonds on the surface of the AT and OAT were detected by a Fourier transform infrared (FTIR) spectroscopy (Nexus, Thermo Nicolet). The morphologies of the AT and OAT were examined using a scanning electron microscope (SEM, JSM–5610LV). Particle size and microstructure were observed by a transmission electron microscopy (TEM) (JEOL JEM-2010, Japan). The BET specific surface area of the samples was determined by BET (Brunauer–Emmett–Teller) methods using a nitrogen adsorption apparatus (AUTOSORB-1, Quantachrome Instruments, USA). The UV–vis diffuse reflectance spectra were measured by a UV–vis spectrophotometer (UV2550, Shimadzu, Japan). $BaSO_4$ was used as the reflectance standard. The contents of Ti and Cu were determined by inductively coupled plasma (ICP) spectrometry (Optima 4300DV, Perkin Elmer Ltd, USA).

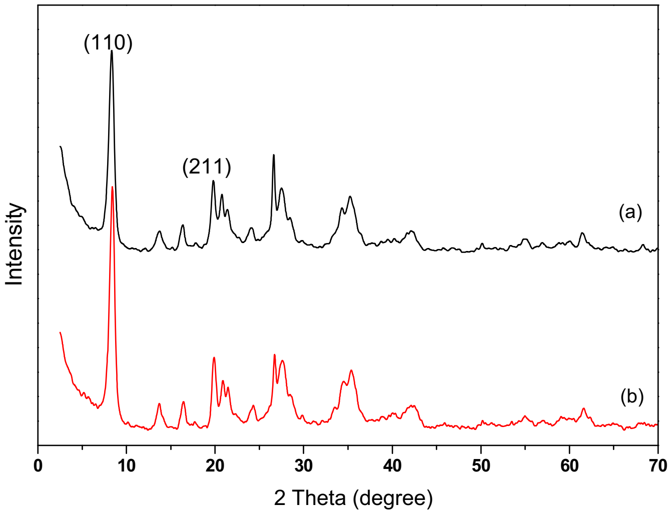

Fig. 1. XRD patterns of (a) the AT and (b) the OAT.

2.5. Photocatalytic activity

A schematic diagram of the experimental system for adsorption and photooxidation is shown in Fig. S1. The experiments were performed in a gas-closed stainless steel photoreactor (capacity 14 L). Two 18 W Hg lamps (F15T8, PHILIPS, Holland) with the maximum light intensity at 365 nm were used as the UV light source and were installed in the center of the photoreactor top. Photocatalyst (2 g) was placed on the bottom of the photoreactor under the two Hg lamps. The desired amount of acetone (20 μL) was injected into the photoreactor with a microsyringe and the fan was turned on at the same time. After the adsorption reached equilibrium, the degradation started with turning on the two Hg lamps. The photocatalytic activities of the catalysts were evaluated by the conversion of acetone and CO_2 in air in the photoreactor. The gas concentrations were measured by a 1412 photoacoustic field gas-monitor (Innova, AirTech Instruments, Denmark) per 5 min.

3. Results and discussion

3.1. Characterization of AT and OAT samples

3.1.1. XRD patterns

The XRD patterns of the AT and the OAT are shown in Fig. 1. The samples display the characteristic peaks of the AT at $2\theta = 8.7°$ (1 1 0) and 20.2° (2 1 1). According to the Bragg equation, the (1 1 0) interplanar spacing of the AT and OAT were 1.014 and 1.039 nm,