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Journal of Molecular Catalysis A: Chemical 284 (2008) 155–160
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

The structural, physical and photocatalytic properties of the mesoporous Cr-doped TiO_2

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Received 26 December 2006; received in revised form 26 November 2007; accepted 6 January 2008

Abstract

A visible-light-active mesoporous Cr-doped TiO_2 photocatalyst with worm-like channels was synthesized using an evaporation-induced self-assembly approach and characterized by X-ray powder diffraction, nitrogen adsorption–desorption, X-ray photoelectron spectroscopy, transmission electron microscope, and UV–vis diffuse reflectance, respectively. The effect of Cr^{3+} doping concentration on the photocatalytic activity of mesoporous TiO_2 was investigated from 0.1 to 1 mol%. The characterizations indicated that the photocatalysts possessed a homogeneous pore diameter of about 8 nm with high surface area of 117 m^2/g and a crystalline anatase pore wall doped by Cr^{3+}. Compared with pure mesoporous TiO_2, the Cr-doped TiO_2 extended the photoabsorption edge into the visible light region. The results of gaseous acetaldehyde photodecomposition showed that mesoporous Cr-doped TiO_2 exhibited higher photocatalytic activities than pure mesoporous TiO_2 and nonporous Cr-doped TiO_2 under visible light irradiation.

Keywords: Cr-doped; Mesoporous TiO_2; Photocatalysis; Acetaldehyde; Photodecomposition

1. Introduction

More recently, the metal-oxide photocatalysts have become a focus of attention due to their possible application to degradation of environmental organic pollutants and the conversion of solar-energy [1–6]. Among the very few photochemically and chemically stable photocatalysts, TiO_2 (P25) is one of the most popular photocatalysts due to its high photocatalytic activity when irradiated by UV light ($\lambda < 400$ nm) [7]. It has also been clarified that the photocatalytic activity of TiO_2 strongly depends on its physical properties, such as crystal structure, surface area, particle size, surface hydroxyls, etc. [8,9]. Of these physical properties, surface area is one of the key factors in enhancing the photocatalytic activity. The larger the surface area is, the more the photocatalytic active sites are, thus enhancing the photocatalytic activity. Mesoporous TiO_2, which displayed better photocatalytic activity than P25 because of its larger surface area, has therefore received much interest in photocatalysis [10–13]. However, pure mesoporous TiO_2 only strongly absorb UV light (rather than visible light), which only accounts for a small fraction of the solar spectrum (<4%). The development of visible light responsive mesoporous TiO_2 has the positive effect on improving the photocatalytic efficiency. In addition, for practical application to decompose indoor organic pollutants, it is necessary to extend the photoabsorption of TiO_2 into visible light region. Thus, exploring visible light absorption, large surface areas and crystalline pore wall mesoporous TiO_2 is significant.

Thus for, extensive researches have been conducted to convert the TiO_2 absorption from the ultraviolet to the visible light region by the ion doping of transition metals [14]. Among these transition metal ions, Cr^{3+} has received much attention because its

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doi:10.1016/j.molcata.2008.01.005

introduction can excellently extend the visible light absorption. In 2002, Palmisano et al. studied the photocatalytic degradation of aliphatic and aromatic compounds in aqueous systems on Cr-doped polycrystalline TiO_2 powder [15]. Afterwards, Gonzalez-Elipe et al. investigated the photocatalytic properties of Cr-doped TiO_2 thin film prepared by ion beam-induced CVD [16]. Zhang et al. studied the photooxidation of XRG (azoic dye) aqueous solution on Cr-doped TiO_2 prepared by a process that combined sol–gel with hydrothermal method. The results showed that Cr-doped TiO_2 effectively improved the photocatalytic activity under visible light irradiation within the optimal doping concentration from 0.15 to 0.2% [17]. Yin et al. synthesized the mesoporous Cr-doped TiO_2 and studied its electrorheological activity [18]. More recently, Yu et al. fabricated mesoporous Cr-TiO_2 photocatalyst and evaluated its activity for photodegradation of methylene blue. The results showed that the photocatalytic activity of mesoporous Cr-doped TiO_2 was higher than that of pure mesoporous TiO_2 [19]. However, so far, there is no systematic study on the effect of the Cr/Ti molar ratio on the acetaldehyde photodecomposition over mesoporous Cr-doped TiO_2 under visible light irradiation.

In present work, mesoporous Cr-doped TiO_2 with worm-like channels was synthesized using an evaporation-induced self-assembly approach. The effect of Cr doping concentration on the photocatalytic activity of mesoporous TiO_2 was investigated from 0.1 to 1 mol%. The photocatalytic decomposition of acetaldehyde over these obtained samples was conducted under UV-light and visible light irradiation.

2. Experimental

2.1. Preparation of catalysts

In a typical synthesis, 0.01 mol of titanium chloride ($TiCl_4$) was added to a solution containing 1 g of pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M = 5800$, Aldrich) and 10 g of ethanol. To this solution, 1×10^{-5}, 5×10^{-5} and 1×10^{-4} mol $Cr(NO_3)_3$ was added for the synthesis of mesoporous Cr-doped TiO_2, respectively. The resulting sol was gelled in an open petri dish at 50 °C in air for 4 days. The as-made bulk samples were then calcined at 400 °C for 3 h in air at the heating rate of 1 °C min^{-1} to remove the surfactant. The calcined samples were labeled according to the Cr-doping content (the pure mesoporous TiO_2 is denoted as MT-0, the mesoporous Cr-doped TiO_2 is denoted as MT-0.1 and so on). The synthesis of the nonporous 0.1 mol% Cr-doped TiO_2 labeled as Cr-TiO_2-0.1 was similarly conducted but without the surfactant of P123.

2.2. Structural characterization

Wide-angle X-ray powder diffraction (XRD) measurements were performed on a Rigaku Ultima III X-ray diffractometer using Cu Kα radiation. Nitrogen adsorption–desorption isotherms were collected on a Micromeritics Tristar-3000 surface area and porosity analyzer at 77 K after the samples had been degassed in the flows of N_2 at 150 °C for 5 h. The Brunauer–Emmet–Teller (BET) surface area was calculated from the linear part of the BET plot ($P/P_0 = 0.1$–0.25). The pore size distribution plots were obtained by using the Barret–Joyner–Halenda (BJH) model. Images of high-resolution transmission electron microscope (HRTEM) were obtained by employing a TECNAI F20 high-resolution transmission electron microscope with a 200 kV accelerating voltage. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB Mark II (VG Company, U.K.). The UV–vis diffuse reflectance spectrum was measured on a UV–vis spectrophotometer (UV-2550, Shimadzu).

2.3. Investigations of photocatalytic properties

The photocatalytic activities of the prepared samples for the oxidation of acetaldehyde in air were examined at room temperature. In a typical process, powder sample (0.1 g) was put on a 4-cm^2 glass groove. The glass with powder photocatalyst was then placed into a 224-ml gastight reactor with a quartz window, filled with air to one atmospheric pressure. Then, acetaldehyde (5 μl of 40% CH_3CHO aqueous solution) was injected into the reactor to generate a high-concentration acetaldehyde gas. The light source for the catalytic reaction was a 300-W Xe arc lamp. The evolved carbon dioxide was detected by a Shimadzu GC-14B gas chromatograph equipped with a methanizer and a FID detector.

3. Results and discussion

3.1. Powder X-ray diffraction analysis

Fig. 1 shows the wide-angle XRD patterns of the samples calcined at 400 °C. Only the single anatase TiO_2 (JCPDS, No. 21-1272) was formed and no chromium oxide impurity phase was detected. Similar results have been reported previously [17]. In fact, Cr^{3+} ions can be easily incorporated into the TiO_2 lattice via displacing Ti^{4+} sites due to their close ionic radius of Ti^{4+} (0.68 Å) and Cr^{3+} (0.64 Å) [20]. In addition, the mean crystalline sizes calculated by the Scherrer equation are summarized in

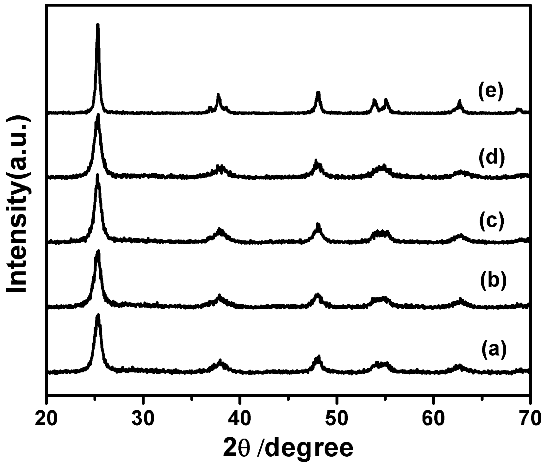

Fig. 1. Wide-angle XRD patterns of mesoporous Cr-doped TiO_2 sample with different Cr^{3+} content: MT-0 (a), MT-0.1 (b), MT-0.5 (c), MT-1 (d) and Cr-TiO_2-0.1 (e).