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Preparation and photocatalytic activity of Fe-doped mesoporous titanium dioxide nanocrystalline photocatalysts

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Abstract

Fe-doped mesoporous titanium dioxide nanocrystalline photocatalysts were prepared by the sol–gel method. The as-prepared samples were characterized with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and N_2 adsorption–desorption measurements. The photocatalytic activities were evaluated by photocatalytic oxidation of acetone in air. It was found that a small amount of Fe dopant in mesoporous TiO_2 powders could obviously enhance the photocatalytic activity, and when the atomic ratio of Fe/Ti was in the range of 0.05–0.25%, the photocatalytic activity of the samples was higher than that of Degussa P25 and un-doped mesoporous TiO_2 powders. This was ascribed to the fact that a small amount of Fe dopant reduced the recombination of photo-generated electrons and holes in the mesoporous TiO_2 powders during heterogeneous photocatalytic reaction.

Keywords: Mesoporous; TiO_2; Anatase; Nanocrystalline; Sol–gel method; Fe-doping; Photocatalytic oxidation; Acetone

1. Introduction

In recent years, in order to solve the increasingly serious problems of environmental pollution, various advanced techniques are being applied in the fields of environmental protection. Semiconductor heterogeneous photocatalysis is a popular technique that has great potential to control aqueous organic contaminates or air pollutants. Among various oxide semiconductor photocatalysts, titanium dioxide has been proved to be the most suitable catalysts for widespread environmental application because of its biological and chemical inertness, strong oxidizing power, non-toxicity and long-term stability against photo corrosion and chemical corrosion [1–4].

The photocatalytic activity of semiconductor is due to the production of excited electrons in the conduction band of the semiconductors, along with corresponding positive holes in the valence band under UV illumination. These energetically excited species are mobile and capable of initiating many photocatalytic reactions, usually, by the production of free radical species at the semiconductor surface. They are unstable, however, and the recombination of photo-generated electrons and holes can occur very quickly, dissipating the input energy as heat [5,6]. In fact, the photocatalytic efficiency depends on the competition between the surface charge carrier transfer rate and the electron-hole recombination rate. If the recombination rate is so fast (<0.1 ns), that there is no enough time for any other reactions to occur [2]. This results in that photocatalyst has no photocatalytic activity. In titania, the photo-generated electrons and holes have relatively long-life (around 250 ns), allowing these species to travel to the crystallite surface [2,3]. It is found that different types of radicals are formed on the surface of TiO_2, the most common radical is OH radical, which is then free to carry out other chemical reactions at the surface [7].

To reduce the recombination of photo-generated electrons and holes, and to extend the light absorption of TiO_2 into visible light region, many researchers used various preparation methods [8–10], different carriers [11,12] and surface modifications [13,14] to prepare highly active photocatalysts. It has been reported that transition metal ions doping can enhance

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the photocatalytic activity of TiO_2. Among various transition metal ions, most researchers found that the Fe^{3+}-doped can enhance photocatalytic activity [2,15].

The well-known method to prepare metal ions doping TiO_2 is based on the sol–gel process via hydrolysis mechanism, which has many advantages, such as, flexible control of pore structures and dopant concentration and a high level of chemical purity [16–18]. Therefore, the sol–gel method is widely used to prepare nano-sized TiO_2 photocatalysts. Fe^{3+}-doped TiO_2 photocatalyst prepared by the sol–gel method has been most extensively examined [19–23], but most of researchers investigated their photocatalytic activity in aqueous solution, while few works were focused on the gaseous photocatalytic reaction, such as the oxidation of acetone in air. In our previous works [24–27], we prepared mesoporous TiO_2 photocatalysts (films and powders) by the sol–gel method and used them to decompose acetone in air. Herein, the Fe-doped mesoporous TiO_2 nanocrystalline powder photocatalysts were prepared by the sol–gel method. The as-prepared powders were characterized with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and N_2 adsorption–desorption measurements. The photocatalytic activity was evaluated by the photocatalytic oxidation of acetone in air and the effects of Fe-doping on the activity were also discussed.

2. Experimental

2.1. Preparation

Fe-doped mesoporous TiO_2 nanocrystalline photocatalysts were prepared by the following method. Tetrabutyl titanate ($Ti(OC_4H_9)_4$ or TBOT) and diethanolamine were dissolved in ethanol. After stirring vigorously for 2 h at room temperature, a mixed solution of water and ethanol was added drop-wise to the above solution with a burette under stirring. The chemical composition of the starting alkoxide solution was $Ti(OC_4H_9)_4:C_2H_5OH:H_2O:NH(C_2H_4OH)_2 = 1:26.5:1:1$ in molar ratio. Finally different amount of ferric nitrate ($Fe(NO_3)_3$) was added to the above precursor titanium sol. The atomic ratios of Fe to Ti, which hereafter was designated as R_{Fe}, were 0, 0.05, 0.25, and 2.5 nominal atomic % (at.%) (as shown in Table 1). The resultant mixed solution was stirred for 2.5 h and then aged for 24 h at the room temperature. The aged wet sols were irradiated under infrared lamp about 48 h to get xerogel. The xerogel were calcined at 773 K for 3 h in the furnace in air to remove organic substances.

2.2. Characterization

The X-ray diffraction (XRD) patterns obtained on a diffractometer (type HZG41B-PC) using Cu Kα radiation at a scan rate (2θ) of $0.05^\circ\ s^{-1}$ were used to determine the identity of any phase present and their crystallite size. The accelerating voltage and the applied current were 15 kV and 20 mA, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on a KRATOA XSAM800 XPS system with Mg Kα source. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the powders was analyzed by nitrogen adsorption in an AUTOSORB-1 (Quantachrome Instruments, USA) nitrogen adsorption apparatus. All the samples and P25 were degassed at 453 K prior to nitrogen adsorption measurements. The BET surface area was determined by multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. The desorption isotherm was used to determine the pore size distribution using the Barret-Joyner-Halender (BJH) method with cylindrical pore [28]. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.994 was used to determine the pore volume and average pore size.

2.3. Measurement of photocatalytic activity

In order to characterize the photocatalytic activity of the as-prepared samples and P25, we choose acetone as a model contaminate chemical. Photocatalytic oxidation of acetone is based on the following reaction [24,29]:

$$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O \qquad (1)$$

The photocatalytic activity experiments on the as-prepared powders and Degussa P-25 for the oxidation of acetone in air were performed at ambient temperature using a 15 L photocatalytic reactor. The catalysts were prepared by coating an aqueous suspension of TiO_2 powders onto three dishes with

Table 1
Effect of R_{Fe} on the average crystallite size, BET surface areas and pore parameters of the as-prepared mesoporous TiO_2 powders

Sample	R_{Fe}	Crystallite size (nm)[a]	S_{BET} ($m^2\ g^{-1}$)[b]	Pore volume ($mL\ g^{-1}$)[c]	Pore size (nm)[c]
P_{25}	–	30.0	63.0	0.060	3.8
a	0	16.2	20.1	0.031	4.4
b	0.05	16.0	23.5	0.040	3.4
c	0.25	14.9	30.3	0.053	3.0
d	2.50	11.0	37.1	0.071	2.8

[a] Average crystalline size of TiO_2 was determined by XRD using Scherrer equation.
[b] The BET surface area was determined by multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3.
[c] Pore volume and average pore size were determined by adsorption volume at $P/P_0 = 0.994$.