ELSEVIER

Journal of Alloys and Compounds 425 (2006) 76–80

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Preparation and photocatalytic property of potassium niobate $K_6Nb_{10.8}O_{30}$

Gaoke Zhang*, Xi Zou, Jie Gong, Fangsheng He, Hao Zhang,
Qiang Zhang, Ying Liu, Xia Yang, Bo Hu

School of Resources and Environmental Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, People's Republic of China

Received 1 November 2005; received in revised form 8 January 2006; accepted 11 January 2006

Abstract

The TB-type potassium niobate $K_6Nb_{10.8}O_{30}$ was synthesized by a simple solid-state reaction method. Scanning electron microscope (SEM) and X-ray diffractometer (XRD) were used to characterize the structure of the photocatalyst. The photocatalyst $K_6Nb_{10.8}O_{30}$ shows high photocatalytic activity to photodegrade acid red G under UV irradiation. The influences of catalyst dosage, initial concentration of acid red G on the photocatalytic reaction were investigated. The kinetics of photocatalytic degradation of acid red G follows the first order kinetics.

Keywords: $K_6Nb_{10.8}O_{30}$; Niobate; Solid-state reaction; Photocatalytic activity; Acid red G

1. Introduction

Dye pollutants from the textile industry are an important source of environmental contamination. Indeed, these effluents are toxic and mostly nonbiodegradable and also resistant to destruction by physico-chemical treatment methods. One difficulty with these methods is that they are not destructive but only transfer the contamination from one phase to another. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove color from textile effluents. Recently much interest has been paid to photocatalytic methods, which cost less money, and don't create secondary contamination. Semiconductor photocatalysis, with a primary focus on TiO_2 [1–4], has been applied to a variety of problems of environmental interest. Although titanium oxide catalysts are capable of decomposing a wide variety of organic and inorganic pollutions and toxic materials [5–7], their reactivity and selectivity are still not enough for large-scale applications.

In the past two decades, many attentions have been paid for finding more efficient photocatalysts, a variety of niobates, such as $K_4Nb_6O_{17}$ [8], Bi_2InNbO_7 [9], $Sr_2Nb_2O_7$ [10], etc., had been extensively studied as a new class of photocatalysts in the field of water splitting, and compounds mentioned as above were all belong to layered niobates. In this paper, we report another new type niobate photocatalyst $K_2Nb_4O_{11}$ used as photodegradating dyes, which assumes a tetragonal tungsten bronze (TB) with space group *P*4/*mbm* (1 2 7), and its molecular formula can be written as $K_{5.75}Nb_{10.85}O_{30}$ or $K_6Nb_{10.8}O_{30}$ according to its crystal structure characteristic [11–12]. The crystal structure of $K_6Nb_{10.8}O_{30}$ is constructed by NbO_6 octahedra, which form some triangle, quadrilateral and pentagonal tunnels. The pentagonal and quadrilateral tunnels are occupied by K cations and the triangle tunnels are occupied by Nb cations [11–12]. Up to now, there are many studies reported on the structures and properties of TB-type niobates, however, the study of the photocatalytic property of TB-type niobates in the field of photodegrading the pollution hardly had been reported yet [11–14]. Although the $K_6Nb_{10.8}O_{30}$ is a kind of substance with known structure, the property of the compound has never been reported and its synthesis method is more complex [11–12] and is studied rarely. In this paper, we prepared the TB-type potassium niobate $K_6Nb_{10.8}O_{30}$ by a simple solid-state reaction method and discuss the photocatalytic property of it for photodegradation of acid red G.

2. Experimental

2.1. Synthesis of the catalysts

The samples of $K_6Nb_{10.8}O_{30}$ were prepared by solid-state reaction method. Analytical grade of K_2CO_3, Nb_2O_5 were used as starting materials. The starting

---

* Corresponding author.
E-mail address: gkzhang@mail.whut.edu.cn (G. Zhang).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.01.016

materials with suitable ratio were mixed and pressed into small pellets with an agate mortar for 30 min, an excess of potassium carbonate (10 mol%) was added to compensate for losses due to volatilization. The small pellets were sintered in a crucible at 1000 °C for 2 h, and then cooled to room temperature. The new samples were prepared for X-ray diffraction (XRD) patterns and experiments by manually grinding with an agate mortar again.

2.1.1. Photocatalytic experiments

The photodegradation of aqueous acid red G was carried out in a 500 ml beaker with constant magnetic stirring. A commercial 20 W UV lamp was used as the light source. Reaction suspension was prepared by adding certain amount of prepared sample into a 150 ml of aqueous acid red G solution. The light intensity was about 0.745 mW/cm^2 measured by using an UV-B radiatometer and the distance between the liquid surface and the light source was about 8 cm. Sampled the solution six times in 2 h during the photocatalytic process, and the concentration of aqueous acid red G were determined by measuring the absorbance at 505 nm with an UV–vis spectrophotometer and a calibration curve. By this method, the conversion percent of acid red G can be obtained in different intervals. The photodegradation rate (X) is given by $X = (C_0 - C)/C_0 \approx (A_0 - A)/A_0$, where C_0 is initial concentration of acid red G, C is concentration at time t, A is the absorbance. The linear relationship between the absorbance at 505 nm (A) and the acid red G (C) (mg/l) can be represented empirically by the equation:

$$A = 0.01C - 0.0003 \tag{2.1}$$

3. Result and discussion

3.1. Characterization of as-prepared samples

3.1.1. XRD patterns analysis

The structure of the $K_6Nb_{10.8}O_{30}$ crystal was determined by X-ray diffraction pattern. X-ray powder diffraction patterns of prepared samples were carried out on a Rigaku D/MAX-RB powder X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 0.1540598 nm) operating at 40 kV and 50 mA, and employing a scanning rate of 0.02° and speed of 3°/min, in the range of 2θ from 5° to 70°. As shown in Fig. 1, the prepared samples consisted of the niobate $K_6Nb_{10.8}O_{30}$ when calcined at 1000 °C for 2 h. The sharp peaks in the XRD patterns indicate a well crystallinity of the prepared samples. The result of XRD patterns confirmed that the compound $K_6Nb_{10.8}O_{30}$ assume a tetragonal tungsten bronze structure with space group *P*4/*mbm* (1 2 7), as confirmed by JCPDS data cards (JCPDS 87-1856). There is a very small amount of niobate $K_3Nb_7O_{19}$ (JCPDS 84-0812) in the sample, which has no remarkable influence on the photocatalytic property of the compound $K_6Nb_{10.8}O_{30}$.

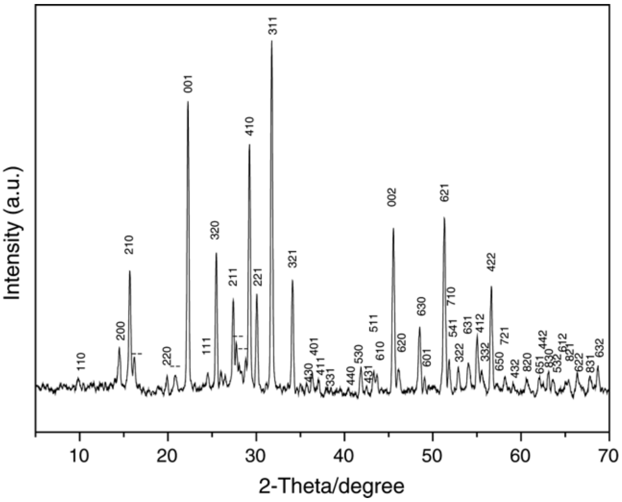

Fig. 1. XRD patterns of the prepared $K_6Nb_{10.8}O_{30}$ at 1000 °C for 2 h; ■ the peaks of $K_3Nb_7O_{19}$.

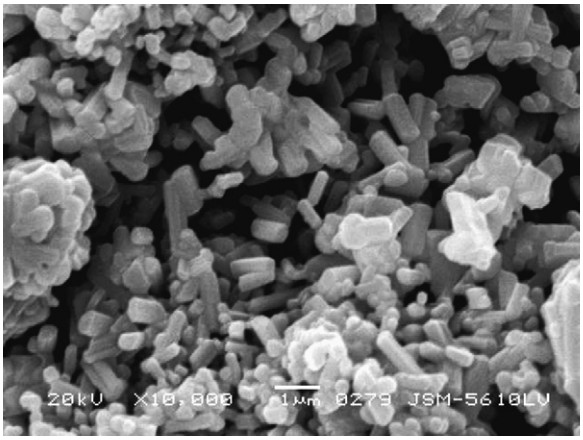

Fig. 2. 10000 × S.E.M. picture of the prepared $K_6Nb_{10.8}O_{301}$.

3.1.2. Scanning electron microscope (SEM) analysis

Particle morphologies of as-prepared powder were estimated using a scanning electron microscope (JSM-5610). As shown in Fig. 2, the sample consists of nearly tetragonal columnar-shaped crystalline particles with an average length of 0.5–1.2 μm and the size of the particles are more uniform.

3.2. Photocatalytic activity of $K_6Nb_{10.8}O_{30}$ photocatalyst

3.2.1. UV–vis spectra changes

The changes in the absorption spectra of acid red G solution during the photocatalytic process by the $K_6Nb_{10.8}O_{30}$ at different irradiation time measured by UV–vis spectrometer (UV-2102/PC) were recorded to determine if any stable chromophoric intermediaters were formed during acid red G degradating. As shown in Fig. 3, before irradiation, the absorption spectra show three distinctive peaks at 505, 330 and 215 nm, respectively and the spectrum of acid red G in the visible region exhibits a main band with a maximum at 505 nm. The peak at 215 nm corresponded to the structure of benzene ring and the peak around 330 nm corresponded to the structure of naphthalene ring, the third peak at 505 nm stand for nitrogen to nitrogen double bond (–N=N–). The decrease of absorption peaks of acid red G at λ_{max} = 505 nm in the figure means the nitrogen to nitrogen double bond was destroyed which indicates a rapid degradation of azo dye. The peaks of benzene ring and naphthalene ring also disappeared gradually in the figure, these indicated that photocatalytic degradation not only destroyed the conjugate system (including –N=N–), but also destroyed the benzene and naphthalene rings.

3.2.2. Effect of the catalyst concentration

Photocatalytic activities of the prepared samples with different concentration were evaluated by the photodegradation