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ScienceDirect

Ceramics International 40 (2014) 15051–15055

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis of spherical Cr_2O_3 nanoparticles by a microwave refluxing method and their photocatalytic properties

Jialiang Su, Hansong Xue*, Ming Gu, Han Xia, Fusheng Pan

College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

Received 2 May 2014; received in revised form 13 June 2014; accepted 23 June 2014
Available online 30 June 2014

Abstract

Spherical chromium oxide (Cr_2O_3) nanoparticles were synthesised by a microwave refluxing method in which potassium chromate (K_2CrO_4) was deoxidised by glucose ($C_6H_{12}O_6$) without using a surfactant or template. The spherical Cr_2O_3 particles were characterised using X-ray diffraction analysis, field-emission scanning electron microscopy, and field-emission transmission electron microscopy. The results showed that the fabricated nanoparticles were perfectly spherical and had a diameter of 50–100 nm. A potential mechanism for the formation of the nanoparticles is proposed. The photocatalytic properties of the Cr_2O_3 nanoparticles were investigated with respect to the degradation of methyl orange. It was found that the spherical Cr_2O_3 nanoparticles subjected to a heat treatment at 800 °C exhibited a higher photocatalytic activity than did the untreated nanoparticles or the nanoparticles heat treated at 400 °C.

Keywords: A. Grain growth; A. Microwave processing; B. Grain size; Cr_2O_3

1. Introduction

Chromium oxide (Cr_2O_3) is used widely in various applications, including as a heterogeneous catalyst [1], a material with high near-infrared reflectance [2], an additive for improving the absorption of hydrogen by Mg [3], and a coating material for thermal protection [4]. The most commonly used method for producing Cr_2O_3 involves deoxidising an alkali dichromate with sulphur, carbon, wood, or ammonium chloride [5]. The size of the resulting Cr_2O_3 particles is usually in the micron range. Further, these particles have an irregular surface morphology [6] that is poorly suited to meet the requirements of high-performance materials, because many fundamental physical and chemical properties of functional materials depend not only on their composition but also on their structure, phase, shape and size. As a result, the synthesis of nano- and microsized materials with large surface areas and high chemical activities has been the subject of active research [7,8].

The most commonly used methods for fabricating Cr_2O_3 nanoparticles are solution-combustion synthesis [9], laser-induced deposition [10], and hydrothermal reduction [11], to name a few. However, these methods are complex and time consuming. In contrast, microwave refluxing is a simple technique for synthesising inorganic materials. In this method, energy can be transferred to materials rapidly using microwave radiation. Therefore, using this method can reduce the processing time as well as the energy cost [12].

In this study, we synthesised spherical Cr_2O_3 nanoparticles using a microwave refluxing method. Further, using comparative studies, the mechanism of formation of the nanoparticles was investigated. Finally, the photocatalytic properties of the synthesised Cr_2O_3 nanoparticles were also studied.

2. Experimental

2.1. Synthesis of spherical Cr_2O_3 nanoparticles

The raw materials used in this experiment were all analytical grade and obtained from Chongqing Chuandong Chemical

*Corresponding author. Tel.: +86 023 65111212.
E-mail address: hsxue@sohu.com (H. Xue).

http://dx.doi.org/10.1016/j.ceramint.2014.06.111
0272-8842/

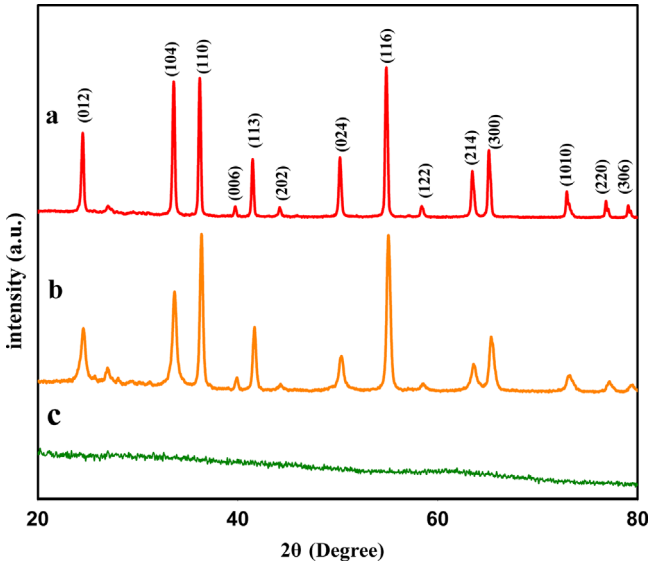

Fig. 1. XRD diffraction patterns of the samples: (a) 800 °C, (b) 400 °C and (c) without heat treatment.

Reagent Co., Ltd., China. Typically, 10 g of K_2CrO_4 (VI), 10 g of glucose ($C_6H_{12}O_6$) and 90 ml of distilled water were mixed under magnetic stirring. Next, nitric acid was added to the uniform mixture until its pH was reduced to 4. The mass fraction of the nitric acid used was 68%. Then, the mixture was transferred to a Teflon flask (150 ml), which was placed in a microwave refluxing reactor (LWMC-205, Shanghai Qing Apple Instrument Co., Ltd.). The power consumed by the microwave was 500 W, and the reaction time was 70 min. After the completion of the reaction, the slurry was allowed to cool naturally to room temperature. The reaction product was collected by centrifugation and subsequently washed several times with distilled water. A green flocculent precipitate was collected after the centrifugation process; this was dried at 60 °C overnight. Finally, samples of the dried precipitate were heat treated at 400 °C and 800 °C for 2 h.

2.2. Characterisation of crystalline structure

The crystalline structures of the samples were characterised through X-ray diffraction (XRD) analysis, which was performed using a Rigaku D/Max-1200X diffractometer and Cu Kα radiation (30 kV, 100 mA). The morphology of the as-prepared sample and the heat-treated ones were observed with a Nova 400 Nano field-emission scanning electronic microscopy (FESEM) system and a Zeiss Libra 200 field-emission transmission electron microscopy (FETEM) system.

2.3. Characterisation of photocatalytic activity

The photocatalytic activities of the Cr_2O_3 nanoparticles were determined by measuring the degradation rate of methyl orange while using the nanoparticles as the catalyst. The degradation rate is directly proportional to the absorbance of methyl orange. Therefore, its absorbance was measured and the degradation rate calculated using the expression $\delta=(A_0-A_t)/A_0$, where A_0 and A_t are the absorbances at 0 min and t min, respectively.

During the measurements, 5 mg of the as-synthesised Cr_2O_3 nanoparticles was added to 10 ml of a methyl orange solution (15 mg/L). The mixture was stirred using an ultrasonic dispersion instrument for 10 min. Then, this mixture was placed in a homemade photocatalytic device. This device consisted of multiple quartz glass tubes, which were placed around an ultraviolet lamp, each at a distance of 15 cm. The methyl orange/nanoparticles dispersion was poured into these glass tubes. The power consumed by the ultraviolet lamp was 15 W. After a set period, the dispersion samples in the tubes were subjected to centrifugation. The absorbances of the supernatants were measured with a 722N spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.). Prior to each photocatalytic experiment, the dispersion samples were stirred again. It was also confirmed that the absorbance of methyl orange did not exhibit any significant changes over time in a controlled trial in the dark in the absence of a catalyst under the same conditions.

3. Results and discussion

Crystal form: The phases of the synthesised nanoparticles were identified through XRD measurements. Fig. 1 shows the XRD patterns of the precursor and the samples calcined at 400 °C and 800 °C. It can be seen in pattern (c) that there are no sharp diffraction peaks, indicating that the as-synthesised, untreated sample had an amorphous structure. On the other hand, the presence of sharp and distinct peaks in patterns (a) and (b) indicated that, after the heat treatments, crystalline nanoparticles with a specific structure were obtained. The intensities of the diffraction peaks in pattern (a) were higher than those of the peaks in pattern (b), indicating that heat treatment at a higher temperature aided the transition to the crystalline form. The diffraction peak (a) could be matched to the rhombohedral Cr_2O_3 structure (JCPDS Card no. 38-1479).

Morphology: The morphology of the as-prepared sample and the heat-treated ones was investigated using FESEM and FETEM. SEM and TEM images of the untreated Cr_2O_3 nanoparticles are shown in Fig. 2(a) and (b), respectively, while those of the Cr_2O_3 nanoparticles heat treated at 400 °C are shown in Fig. 2 (c) and (d), respectively. It can be seen clearly that the synthesised Cr_2O_3 nanoparticles were nearly spherical. When the heat treatment temperature was increased to 800 °C, the obtained nanoparticles were uniform in size and shape (see Fig. 2(e) and (f)). Hence, it can be summarised that a post-microwave-refluxing heat treatment at high temperatures results in the synthesis of uniform spherical Cr_2O_3 nanoparticles. However, further research is necessary to understand the changes that occur in the nanoparticle morphology during the heat treatment.

Formation mechanism: Fig. 3 shows the formation process of the Cr_2O_3 nanoparticles prepared by the microwave refluxing method. The $Cr(OH)_3$ nanoparticles were formed by a redox reaction of K_2CrO_4 and glucose ($C_6H_{12}O_6$) [13]. Under microwave irradiation, the reaction rate was high, resulting in