

2,4-Dichlorophenoxyacetic acid (2,4-D) photodegradation using an M^{n+}/ZrO_2 photocatalyst: XPS, UV–vis, XRD characterization

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Received 10 November 2006; received in revised form 16 December 2006; accepted 19 December 2006

Available online 23 December 2006

Abstract

Zirconium oxide materials doped with transition metals (Mn, Fe, Co, Ni and Cu) were synthesized using sol–gel methods. The powders, which were obtained, were characterized by XPS, XRD, UV–vis spectroscopy and nitrogen adsorption.

The photodegradation of 2,4-dichlorophenoxyacetic acid (2,4-D), a herbicide used in agricultural applications, was used as a test reaction to study the activity of the compounds synthesized. Photodegradation studies were performed using a lamp radiating light with a UV wavelength of 254 nm. Characterization studies showed a predominance of the tetragonal phase of zirconium oxide for all of the samples studied. The values obtained for the forbidden energy level E_g fall in a range between 3.6 and 5.5 eV. BET surface areas were found to be in a range between 55 and 80 m²/g. The concentration of the metals is small and in the case of Ni it could not be detected. Samples calcined at 400 °C used in the photocatalytic study showed the highest activity. Mn/ZrO₂ was the most active photocatalyst used. A 70% conversion of 2,4-D was obtained in the first hour. This can be compared to a conversion of only 30% in the absence of Mn/ZrO₂.

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Keywords: Photocatalysis; 2,4-Dichlorophenoxyacetic acid; XPS; Band gap; Tetragonal zirconia

1. Introduction

Dichlorophenoxyacetic acid (2,4-D) is one of the herbicides most used in Mexico. Its primary function is to control wide leaf weeds present in cereal crops [1–3]. It is considered to be potentially dangerous to both animals and humans. Its biodegradability is extremely low and it has been detected as a major contaminant in effluents from both subterranean and superficial waters [4,5]. A method, which has been recently used to destroy these types of compounds involves ozonation [6,7]. However, the high cost of energy required in the process

has lead to new alternatives to eliminate these compounds. 2,4-D forms part of a group of compounds (which also include chlorophenols) in which its degradation can be more conveniently employed using heterogeneous photocatalysis [8,9]. Using this process, aggressive oxidation can lead to complete mineralization.

A large number of studies in photocatalysis performed during the last decade have shown that this technology results in the most effective treatment of contaminated water [10]. Titania has up to now, been the most effective photocatalyst used in solid–liquid systems [8,11–13]. This is primarily due to its commercial availability. However, commercial titania has certain characteristics (low surface areas, mixture of crystalline structures, to name a few) which may limit its use. On the other hand, the modification of titania may lead to poor results [14].

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For this reason it might be useful to explore the use of alternative oxide semiconductors whose properties may be superior to those of TiO_2 .

In this work we analyze the effect of modifying ZrO_2 semiconductor with first transition series cations trying to correlate the modification of the electronic properties with the catalytic activity (Fig. 1).

2. Experimental

2.1. The synthesis of pure ZrO_2 sol–gel

The synthesis was performed in the following manner: 6 mL of deionized water was mixed with 61 mL of *tert*-butyl alcohol (Sigma–Aldrich, 99.7%) under continual stirring for 10 min. Concentrated HNO_3 was added until a pH of 3 was obtained. The solution was heated to a temperature of 70°C and was maintained at that temperature for a period of 10 min. It was later decreased to 60°C while a dropwise addition of 39 mL of zirconium *n*-butoxide was performed (Sigma–Aldrich, 80%). Following the addition, the alkoxide mixture was maintained at a temperature of 70°C for 24 h under continual agitation and total reflux. This was followed by evaporation of the solvent and drying at 80°C in an oven for 24 h (Fig. 2).

For the case of M^{n+} modified ZrO_2 catalysts where $\text{M} = \text{Mn}$, Fe , Co , Ni , Cu , a quantity of nitrate corresponding to that of the ionized metal (Sigma–Aldrich, 99% purity) was dissolved in deionized water such that the concentration of the resulting solution was 1 mol% dispersed in the sol–gel zirconium oxide.

The materials obtained by this method were ground and calcined in air at 300, 400, 500 and 600°C for 12 h. A temperature increase rate of $2^\circ\text{C}/\text{min}$ was used.

2.2. Characterization

2.2.1. XPS spectroscopy

The XPS experiments were performed using $\text{Al K}\alpha$ radiation (15 kV, 20 mA) following outgassing of the samples in a pretreatment chamber to a vacuum of better than 10^{-7} Torr. The spectra were recorded with a vacuum, which was better than 10^{-9} Torr and the energy scale was referenced to the spurious carbon C 1s signal at 284.6 eV.

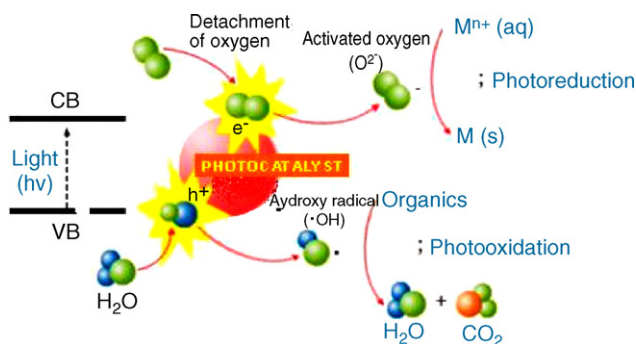


Fig. 1. Scheme of the photocatalytic process.

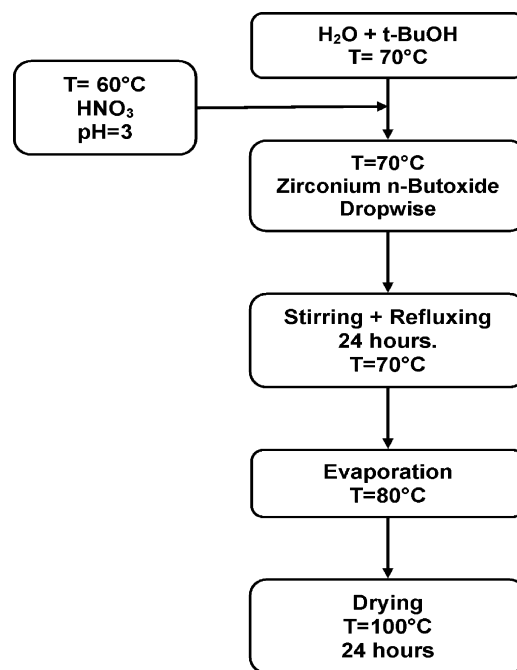


Fig. 2. Flow diagram of the sol–gel synthesis.

2.2.2. UV–vis spectroscopy

UV–vis spectra were performed using a Cary-1 (Varian) spectrophotometer. The band gap of a material can be estimated from the adsorption edge wavelength of the interband transition. The most accepted method for determining the band gap energy values of an insulator or semiconductor is by plotting the square root of the Kubelka–Munk function multiplied by the photon energy versus the photon energy and extrapolating the linear part of the rising curve to zero. For each material the energy of the forbidden band (E_g) was calculated in accord with the following equation:

$$E_g (\text{eV}) = \frac{1239b}{-a} \quad (1)$$

where a and b are coefficients which were linearized in the appropriate region of the spectrum.

2.2.3. XRD patterns

In order to analyze the crystal phases of the samples, measurements were performed using X-ray diffraction. A D-5000 diffractometer using $\text{Cu K}\alpha$ radiation and a graphite monochromator was used in the diffracted beam to perform these experiments. XRD patterns were collected in the θ – 2θ mode with an step angle of 0.03° falling 2θ in a range between 4° and 70° and $t = 0.3$ s.

2.2.4. Photoactivity

The catalytic photodegradation studies were performed using the following procedure: 100 mg of photocatalyst were placed in 100 mL of a solution of 2,2,4-dichlorophenoxyacetic acid (300 ppm). In order to insure adsorption of the molecule on the photocatalyst, the suspension was maintained under continual stirring (without light) for 30 min under an air flow

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