Chemical Engineering Journal 213 (2012) 286–294

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Innovative photocatalytic degradation of polyethylene film with boron-doped cryptomelane under UV and visible light irradiation

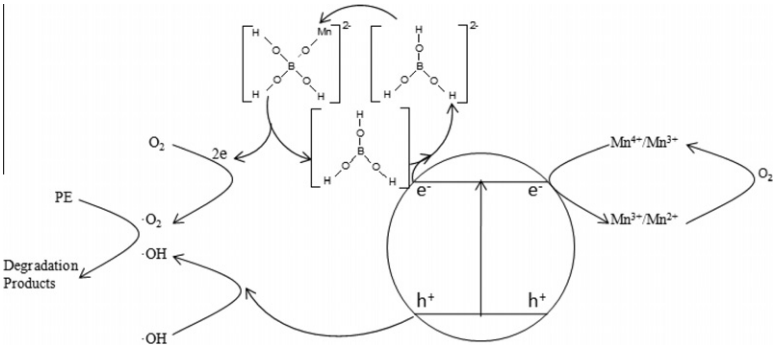
Guanglong Liu [a], Shuijiao Liao [b], Duanwei Zhu [a,*], Yumei Hua [a], Wenbing Zhou [a]

[a] Laboratory of Plant Nutrition and Ecological Environment Research, Centre for Microelement Research of Huazhong Agricultural University, Wuhan 430070, China
[b] College of Basic Sciences, Huazhong Agricultural University, Wuhan 430070, China

HIGHLIGHTS

- The boron doped cryptomelane was successfully prepared by a sol–gel method.
- B-OMS-2 exhibited greater light absorption property than that of OMS-2.
- Higher weight loss and greater texture change were obtained in PE-B-OMS-2 sample.
- A plausible mechanism was proposed on the basis of experimental results.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 June 2012
Received in revised form 27 September 2012
Accepted 28 September 2012
Available online 12 October 2012

Keywords:
Photocatalytic degradation
Polyethylene film
B-doped OMS-2
Mechanism research

ABSTRACT

The boron doped cryptomelane prepared by a sol–gel method was employed as photocatalyst for the degradation of polyethylene (PE) film under the UV and visible light irradiation. The cryptomelane (OMS-2) and boron doped cryptomelane (B-OMS-2) were characterized by X-ray diffraction (XRD), laser particle size analysis, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), UV–vis spectroscopy and porosimeter analysis. The results indicated that the particle size, crystallinity of the boron doped OMS-2 increase, whilst surface area increase compared to regular OMS-2. FTIR and Raman results suggested that the dopants were dispersed into the framework of manganese oxide. The existence of interstitial boron in doped cryptomelane was confirmed by XPS. The UV–vis spectra showed that B-OMS-2 sample exhibited greater absorption property than that of OMS-2 sample after boron doping. In order to explore the application of these manganese oxides in environmental remediation, an attempt has been made for the degradation of polyethylene films using synthesized particles as catalyst in the form of PE-OMS-2 and PE-B-OMS-2 composite films under the UV–vis light irradiation. Higher PE weight loss rate and greater texture change could be obtained in the system of PE-B-OMS-2 composite in comparison with PE and PE-OMS-2 composite film, which indicated that the B-OMS-2 catalyst made the photodegradation of PE film more effective, and B-OMS-2 showed a higher catalytic activity than the regular OMS-2 under UV light irradiation. Compared to the UV light irradiation, no obvious change was detected under the visible light irradiation. Finally, the mechanism of degradation of composite film was also discussed.

* Corresponding author. Tel.: +86 27 87287184; fax: +86 27 87397735.
E-mail address: zhudw@mail.hzau.edu.cn (D. Zhu).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.09.105

1. Introduction

Manganese oxides as the third most abundant transition metal in the earth crust were able to degrade a number of organic pollutants in soils and sediments [1]. Due to the high redox potential [2], manganese oxide was considered as a kind of the important oxidants or catalysts in facilitating organic pollutant transformation and organic matter decomposition [3]. Land-born natural Mn ores, synthetic nascent state Mn oxides, and materials coated/modified with Mn oxides have been tested as scavenger to remove Pb^{2+}, Cd^{2+}, Cu^{2+} [4] and organic pollutant [5–7]. In many kinds of manganese oxides, cryptomelane-type manganese oxide (OMS-2) is particular importance because its structure is the octahedral molecular sieves [8] and cryptomelane has been reported to have excellent catalytic properties [9], and has been extensively tested in toluene [5], phenol heterogeneous oxidation [10] and 2,4-dichlorophenoxyacetic acid photocatalytic degradation [11].

In order to improve the electronic and catalytic properties of cryptomelane-type manganese oxide, transition metal cations were used to replace K^+ in the tunnel mainly by post-ion-exchange [12–15]. For example, substitution of K^+ by Ag^+ in the K-OMS-2 materials resulted in the formation of Ag–OMS-2, which was more promising as environmentally benign and efficient oxidation catalyst [16,17]. However, the use of metal doped manganese oxide for environmental remediation can lead to possible toxicity due to leakage of the metal ion into the environment [18]. For the semiconductor oxide, using anion doing to improve the catalytic activity has been reported by many researchers. However, to our best knowledge, anion doping to improve the photocatalytic activity of manganese oxide has been not reported.

In this work, firstly, a sol–gel method was employed to synthesize OMS-2 and B-doped OMS-2. The OMS-2 and B-OMS-2 are characterized by means of XRD, laser particle size analysis, Raman spectroscopy, XPS, FTIR, UV–vis spectroscopy and porosimeter analysis in order to determine their structural and optical properties. Secondly, agriculture plastic waste such as polyethylene film disposal has been recognized as a worldwide environmental problem. A large portion of plastic film was left on the field or burnt uncontrollably by the farmers, emitting harmful substances with the associated negative consequences to the environment. Many works has reported that the polyethylene polymers could be degraded by TiO_2 as catalyst [19,20]. However, the widespread technological use of TiO_2 is impaired by its wide band gap (3.2 eV for the anatase phase), which can only be activated by UV light [21]. The band gap energy of manganese oxide was 0.26–0.7 eV, which can be activated under both UV and visible light [22]. Therefore, an attempt has been made for the photocatalytic degradation of polyethylene films using manganese oxides as catalyst. A novel modified embedding route was employed to synthesize the PE-OMS-2 and PE-B-OMS-2 composite film and the application of the OMS-2 and B-OMS-2 for the treatment of polyethylene film was evaluated in this study.

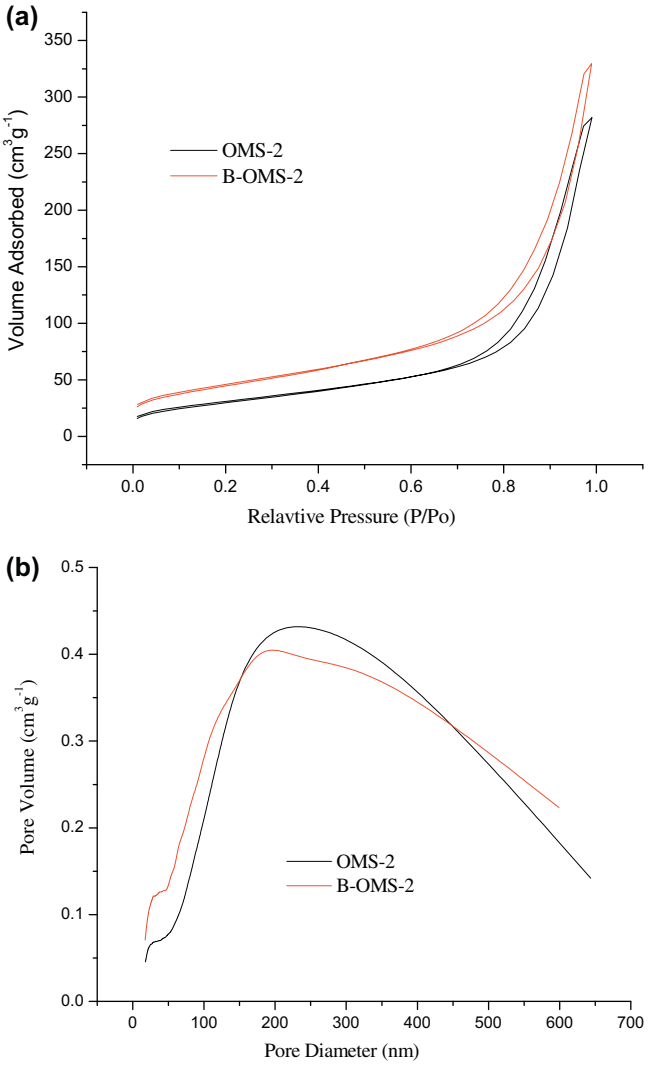


Fig. 1. (a) Nitrogen adsorption–desoprtion isotherms and (b) the corresponding pore size distribution of OMS-2 and B-OMS-2.

2. Materials and methods

2.1. Chemicals

PE (grade-LD103) was purchased from Yanshan Petrochemical Company Ltd. The average molecular weight (Mw) was about 100,000. $MnCl_2{\cdot}4H_2O$ (AR grade), CH_3COOH (AR grade), $KMnO_4$ (AR grade), H_3BO_3 (AR grade) and cyclohexane (AR grade) were supplied from Guoyao Chemical Co. (Shanghai, China). All chemicals were used without further purification and deionized water was used in all the experiments.

Table 1
N_2 physisorption and Mn average oxidation state (AOS) determination results for the OMS-2 and B-OMS-2 samples.

Material	S_{BET}($m^2\ g^{-1}$)[a]	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (Å)	Average oxidation state (AOS)[a]	Crystal size (nm)[b]	Mean particle diameter (μm)
OMS-2	138.8	0.436	154.8	3.756	16.1	99.12
B-OMS-2	206.4	0.510	124.7	3.672	13.2	61.54

[a] Reported by Zhang et al. [31].
[b] Based on XRD using Scherrer's equation: $D = 0.9\ \lambda/(B \times \cos\theta)$, where $\lambda = 0.154$ nm and B = full width at half maximum (FWHM) of the highest peak.