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ScienceDirect
Journal of Hazardous Materials 149 (2007) 460–464
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Detoxification reactions of sulphur mustard on the surface of zinc oxide nanosized rods

G.K. Prasad *, T.H. Mahato, Beer Singh, K. Ganesan, P. Pandey, K. Sekhar

Defence Research and Development Establishment, Jhansi Road, Gwalior, India

Received 9 February 2007; received in revised form 2 April 2007; accepted 3 April 2007
Available online 6 April 2007

Abstract

Detoxification reactions of sulphur mustard, a deadliest chemical warfare agent were studied on the surface of zinc oxide nanorods at room temperature ($32 \pm 2\,^{\circ}C$) and the data was compared with that of the bulk ZnO. Prior to the reaction, the nanorods of zinc oxide were synthesized by the hydrothermal method and subsequently characterized by XRD, SEM, TG, N_2 BET, FT-IR. The data revealed the formation of nanorods with diameter ranging from 100 nm to 500 nm with length in microns. Obtained nanomaterial along with bulk ZnO were tested as reactive sorbent for the detoxification of sulphur mustard. Reaction was monitored by GC-FID technique and the reaction products were characterized by GC–MS. Data explores the role of hydrolysis and elimination reactions in the detoxification of sulphur mustard and it also reveals that zinc oxide nanorods and bulk ZnO show the half lives of 8.48 h, 24.75 h in the first 12 h and 122.47 h, 177.29 h from 12 h to 48 h of the reaction.
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Keywords: Sulphur mustard; Chemical warfare agent; Zinc oxide; Detoxification and hydrothermal method

1. Introduction

Application of nanosized inorganic oxide materials as reactive sorbents has been a promising approach for the decontamination of chemical warfare (CW) agents [1–4]. Strong adsorbability and enhanced reactivity towards the toxicants make them the potential materials for the decontamination applications. These intriguing properties within the above materials are expected to be aroused owing to the high surface area due to smaller particle size and the reactive sites tailored in the form of edge and corner defects, unusual lattice planes, etc. Most likely, these active sites react in a stoichiometric fashion, thereby rendering the adsorbed toxic agents to non-toxic ones and the reactions are analogous to their solution behaviour [5,2].

Recent investigations have explored the promising decontamination applications of nanosized metal oxides such as AP-MgO, AP-Al_2O_3 and AP-CaO [6–11]. They possessed enhanced chemical reactivity towards CW agents including sulphur mustard, which undergo hydrolysis and elimination reactions on the surface of nanoparticles and the same was illustrated by MAS-NMR data. Especially sulphur mustard reacts with AP-MgO, AP-Al_2O_3 and AP-CaO with half lives of 17.8 h, 6.3 h and 8.5 h, respectively, at room temperature yielding the non-toxic elimination and hydrolysis products [12–15]. Although, they have the capability to decontaminate CW agents within few hours of duration, the search for newer and more efficient materials is still going on to ensure the preparedness and enhance the confidence levels regarding safety against the CW agents.

On the other hand, ZnO nanomaterials were found to have interesting applications such as surface acoustic wave filters [16], photonic crystals [17], light emitting diodes [18], photo detectors [19], varistors [20], gas sensors [21], solar cells [23] and catalysts. Recently, one of the variants of ZnO nanomaterials, i.e., ZnO nanorods (ZnO NR) have been synthesized by the hydrothermal method and were used for sensing [22] and catalytic applications [24]. Similar materials have also been used for the decontamination of dimethyl methyl phosphonate (DMMP), a well-known simulant for nerve agents [24,25]. Inspired by these applications, we have attempted to study the decontamination reaction of sulphur mustard (HD) on the surface of ZnO nanorods. After their synthesis, the sample was characterized by SEM, XRD, TG, FT-IR, N_2 BET and then the reactions were monitored by GC and the reaction products were characterized by GC–MS.

* Corresponding author.
E-mail address: gkprasad@lycos.com (G.K. Prasad).

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doi:10.1016/j.jhazmat.2007.04.010

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate, hexamethylenetetramine (HMTA), acetonitrile, chloroform and ZnO were obtained from S.D. Fine Chemicals India Pvt. Ltd. Sulphur mustard of 99% (GC assay) purity was synthesized in our laboratory.

2.2. Characterization

XRD patterns were obtained in an X Pert Pro Diffractometer, Panalytical, Netherlands, using Cu Kα radiation. SEM investigations were carried out on a Philips instrument. N_2 BET measurements were done on Autosorb 1C of Quantachrome, USA make. Subsequently, thermograms were recorded on TGA-2950, TA instruments, USA and the IR data was acquired on Perkin-Elmer FT-IR (Model 1720X) of USA. The Nucon 5700 gas chromatograph equipped with FID detector and OV 17 column (30 m length, 0.5 mm i.d.) was used for the degradation kinetics of HD. Whereas, HP Agilent GC–MS system (5973 Inert) was used for the characterization of reaction products.

2.3. Synthesis of zinc oxide nanorods

Prior to the reaction studies, the zinc oxide nanorods were synthesized by the hydrothermal method as per a reported procedure [26]. For this purpose, the aqueous solution of zinc nitrate was added to the hexamethylene tetramine solution in a conventional reaction flask equipped with a reflux condenser. The reaction temperature was maintained at 98 °C and the reaction was continued for 20 h. Thereafter, the obtained materials were filtered and washed meticulously with ultrapure water. Subsequently, the material was dried at room temperature overnight and at 50 °C for 4 h. Obtained materials, ZnO nanorods along with bulk ZnO were used to study the reaction with HD at room temperature (32 ± 2 °C).

2.4. Reaction of sulphur mustard with ZnO nanorods

For this purpose, 100 μL of chloroform solution having 5 μL of HD was added to 300 mg of the above aggregate powder and the remaining HD was extracted by 5.0 mL of acetonitrile at periodic intervals of time until 48 h to study the kinetics of degradation on the surface of ZnO NR. Thereafter, the extracted solutions were analyzed by GC-FID at isothermal conditions at 110 °C and then the reaction products were characterized by GC–MS.

3. Results and discussion

Hydrothermal treatment of the aqueous solutions composed of zinc nitrate and hexamethylene tetramine at 98 °C facilitated the formation of ZnO nanorods. Formed nanorods were characterized by scanning electron microscopy and the electron micrographs are shown in Fig. 1a and b. The morphology

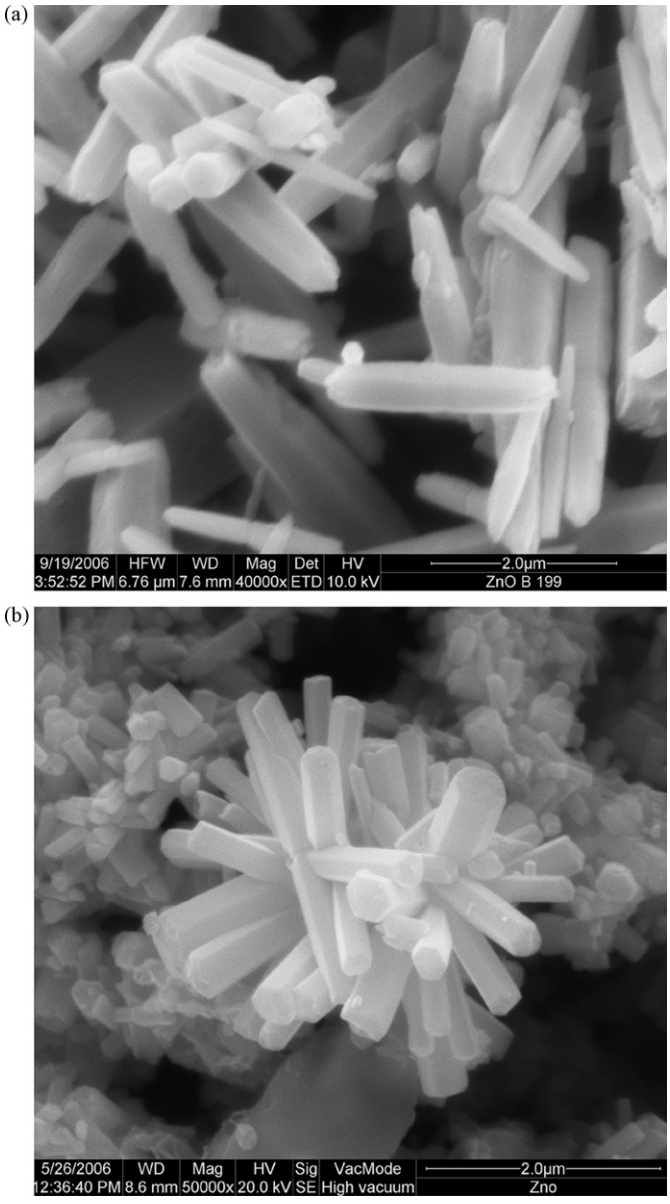

Fig. 1. Scanning electron micrographs of the ZnO nanorods with different orientations.

depicts the rod like nanostructures aligned in an irregular manner while they are found to be stacking at their tips thus showing typical structures where rods are arranged in the form of flowers (Fig. 1b) and this stacking phenomenon can be ascribed to the polar nature of the ZnO surface and the matching lattice structure. Moreover, these rods exhibit the hexagonal shape with diameter ranging from 200 nm to 500 nm and the length ranging from 500 nm to 3 μm (Fig. 1a).

Thereafter, the materials were characterized by X-ray diffraction technique in order to confirm the formation of ZnO and the same is apparently shown in Fig. 2. Bragg peaks appears at 31.775° 2θ, 34.425° 2θ, 36.275° 2θ and 47.625° 2θ which can be ascribed to the presence of (1 0 0), (0 0 2), (1 0 1) and (0 0 2) diffraction peaks. The data reveal the formation ZnO hexagonal shaped nanorods with wurtzite structure and the same was consistent with previously reported data [26]. On the other hand,

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