Arabian Journal of Chemistry (2014) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Adsorption of diazinon and fenitrothion on nanocrystalline magnesium oxides

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Received 9 July 2013; accepted 4 January 2014

KEYWORDS

Nanocrystalline;
Magnesium oxide;
Adsorption;
Diazinon;
Fenitrothion

Abstract Nanocrystalline magnesium oxide was prepared by the sol–gel method from magnesium methoxide and characterized by Fourier transform infrared spectroscopy, thermal analysis, X-ray powder diffraction and transmission electron microscopy. Sol–gel derived nanocrystalline magnesium oxide along with a commercial nanocrystalline magnesium oxide was used as adsorbents to study the adsorption of two common, organophosphorous pesticides, diethoxy-[(2-isopropyl-6-methyl-4-pyrimidinyl)oxy]-thioxophosphorane (diazinon) and dimethoxy-(3-methyl-4-nitrophenoxy)-thioxophosphorane (fenitrothion). Adsorption of diazinon and fenitrothion on the sol–gel derived, and commercial nanocrystalline magnesium oxides was studied using UV–vis, FT-IR and ^{31}P NMR spectroscopies. The effect of hydroxyl groups on edge/corner and flat panel of magnesium oxide in adsorption of diazinon and fenitrothion was investigated. The results showed that the adsorption of diazinon on the sol–gel derived nanocrystalline magnesium oxide is destructive whereas on commercial one is non-destructive. Commercial nanocrystalline magnesium oxide showed higher activity in the adsorption of fenitrothion than the sol–gel derived, and adsorptions on both nanocrystalline magnesium oxides are destructive.

1. Introduction

The ultrafine nanocrystalline metal oxide powders have captured attention of scientists due to their potential applications in catalysis (Velmurugan et al., 2012), adsorption (Anupam et al., 2011), biomedical science, nanodevices, sensors and dye-sensitized solar cell (Al-Owais, 2013; Jeevanandam, 2009). The fascinating behavior of nanomaterials in comparison to bulk materials have been correlated mainly to the high surface area, large number of defects, morphology in addition to pore structure and hydroxyl groups on the surface of oxides (Korotcenkov, 2008; Oh et al., 2007). Although the curial role of surface hydroxyl groups on behavior of nanooxides has been raised by several authors and investigated to some extent, it seems additional work is required for clarification and deeper understanding of their role in adsorption (Martin et al., 2005). Furthermore, it is well-known that the surface of nanooxides powders can be endowed with hydroxyl groups by the low temperature processing technique (Bailly et al., 2005). In

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2014.01.002

Please cite this article in press as: Armaghan, M., Amini, M.M. Adsorption of diazinon and fenitrothion on nanocrystalline magnesium oxides. Arabian Journal of Chemistry (2014), http://dx.doi.org/10.1016/j.arabjc.2014.01.002

this context, low temperature and soft chemical methods of metal oxides' processing, such as the sol–gel have been subject of extensive studies (Jeevanandam, 2009).

Among many metal nano-oxides, magnesium oxide with strong basic properties is unique and has a wide range of applications, including refractory industry, support for metal catalysts, a base catalyst in organic reaction, adsorbent for toxic compound, electronic device and optic (Niederberger and Garnweitner, 2006). Interestingly, for each application a specific processing method which fulfills the properties of magnesium oxide is required. For catalytic and adsorptive applications, nanocrystalline MgO should be prepared with especial crystal morphologies. Such a magnesium oxide possesses multitude surface sites with enhanced surface chemical reactivity, such as crystal corners, edges, or ion vacancies and defects. Residual surface hydroxides can also raise the rich surface chemistry exhibited by nanocrystalline MgO (NC-MgO), and in recent years became the most important influential parameter in the chemistry of ultrafine nanocrystalline MgO powders (Utamapanya et al., 1991; Itoh et al., 1993). The surface chemistry is generally attributable to Lewis acid, Lewis base and Brönsted acid sites of varying coordination, that is, metal cations, oxide anions, and surface-bound OH groups. Nanocrystalline MgO can be especially effective as an adsorbent. This ultrafine powder, in particular, has shown a unique destructive chemisorption capability toward toxic chemical agents (polar organic chemicals). The adsorptive properties of nanocrystalline MgO are diverse and studies have been reported on adsorption of pyridine, phosphorus compounds, sulfur trioxide, and others (Narske et al., 2002; Carnes et al., 2002; Wagner et al., 1999; Stark et al., 1996; Koper et al., 1997). It has shown mechanistically that the heterogeneous reaction of nanocrystalline MgO with pesticide occurs by hydrolysis reactions. The resulting hydrolysis products containing the heteroatom would bind strongly to active sites on nanocrystalline MgO (Lin and Klabunde, 1985; Mishakov et al., 2005; Stoimenov et al., 2003). The surface composition of nanocrystalline MgO has been widely studied because of its effective role in the adsorptive process. There has been some discussion on the type of surface sites on nanocrystalline MgO (Kim et al., 2002; Chizallet et al., 2006). However, data mostly concerning fundamental textural characterization of the surface and the interface are very scantly and mainly limited to the surface data (Kim et al., 2002; Chizallet et al., 2006). Therefore, a study of the relationship between acidic and basic surface sites, coordinatively unsaturated Mg^{+2} ions and stretching vibrational frequencies of the hydroxide groups in crystalline structure of nanocrystalline MgO will be interesting and beneficial. Furthermore, classification of OH types on the surface of nanocrystalline MgO can facilitate the interpretation of adsorptive reaction mechanism in general and destructive adsorption of organophosphorus pesticides in particular (Klabunde et al., 1996; Utamapanya et al., 1991; Itoh et al., 1993; Chizallet et al., 2007).

The aim of this study is to investigate the influence of the sol–gel derived nanocrystalline magnesium oxide on adsorption of diazinon and fenitrothion. In this context, nanocrystalline magnesium oxide was prepared from magnesium methoxide, and after characterization used as a sorbent to adsorb aforementioned pesticides and the result was compared with commercial magnesium oxide.

2. Experimental

2.1. Regents and materials

All chemicals were obtained from the Merck Chemical Company (Darmstadt, Germany) with highest available purity. The commercial nanocrystalline MgO (NanoActive®MgO, CM-MgO) was purchased from the NanoScale Company (www.NanoScaleCorp.com, US) and calcined at 500 °C prior to use. Methanol was dried and distilled over magnesium turning before use.

2.2. Physical measurements

Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1}) were recorded on a 4600 FT-IR spectrometer (Shimadzu, Japan). The samples were pressed to a thin disk with KBr before measurements. UV–vis spectra in the range of 200–800 nm were recorded on a Shimadzu 2100 spectrophotometer at room temperature. The ^{31}P NMR spectra were recorded at room temperature in hexane on a Bruker AVANCE 300-MHz instrument (Bruker, Germany) operating at 121.44 MHz. X-ray powder diffraction analysis (XRD) was performed with Cu-$K\alpha$ radiation on a Philips-PW 17C X-ray diffractometer (Philips, Netherlands). The diffractogram was recorded in 2θ 5–80° at a rate of 3°/min. The specific surface area of the NC-MgO was determined from the nitrogen adsorption at −196 °C using the Brunauer-Emmett-Teller (BET) technique with an ASAP 2000 apparatus (Micromeritics, US). Prior to adsorption calculations, the sample weight was corrected for any weight loss due to degassing or drying. Thermal analysis was carried out on a STA-503 instrument (BAHR, Germany) under ambient conditions. Particle size was estimated from a transmission electron microscopy (TEM) image. TEM image was obtained using a CM-200 FEG instrument (Philips, Netherlands).

2.3. Preparation of nanocrystalline MgO (NC-MgO)

The sol–gel derived nanocrystalline MgO (NC-Mg) was prepared from magnesium methoxide according to the earlier report with slight modification (Heidari et al., 2009). Magnesium methoxide, the precursor for the preparation of the sol–gel derived nanocrystalline MgO, was synthesized by direct reaction of magnesium ribbon and dry methanol in the presence of a small amount of iodine at refluxing temperature. After consumption of magnesium, magnesium methoxide solution in methanol was filtered to remove unreacted magnesium. The synthesis of magnesium methoxide and filtration process were carried out in an inert atmosphere to prevent hydrolysis of magnesium methoxide and formation of undesired MgO. Magnesium methoxide was crystallized from filtrated solution at −20 °C. The well crystallized magnesium methoxide was collected by filtration in an inert atmosphere using a frit-filter and then dried under reduced pressure to obtain white magnesium methoxide powder. The prepared magnesium methoxide was exposed to air with 25% of humidity at 23 °C for 24 h and then the resulted gel was calcined at 500 °C for 3 h. The prepared nanocrystalline MgO was stored in the vacuum desiccator for further use. Prepared material was characterized by FT-IR, XRD, TGA-DTA, TEM and BET surface area analyzer.

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