



Natural silk supported manganese dioxide nanostructures: Synthesis and catalytic activity in aerobic oxidation and one-pot tandem oxidative synthesis of organic compounds



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ABSTRACT

Manganese dioxide nanostructures were coated on natural silk (MnO_2 @silk) by simple immersion of the silk fibers into a KMnO_4 aqueous solution. The silk was found to act as a *in situ* reducing agent and substrate in aqueous KMnO_4 solution for the heterogeneous production of MnO_2 nanostructures. The structure of synthesized catalyst was characterized by X-ray diffraction (XRD), flame atomic absorption spectroscopy (FAAS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) analysis. The catalytic activity of the MnO_2 @silk was examined in the aerobic oxidation of alkyl arenes, alcohols, and oximes to their corresponding carbonyl compounds and a one-pot tandem oxidative two-component reaction of aromatic hydrocarbons of petroleum naphtha in the absence of any other oxidizing reagent or initiator.

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1. Introduction

Biopolymers, as common structural elements of biological systems, have highly specialized properties because of their complex three-dimensional structures. Natural polyamino acid biopolymers (polypeptides or proteins) in organisms are synthesized from combinations of amino acid ($-\text{NH}-\text{CHR}-\text{CO}-$) and imino acid ($-\text{NR}^1-\text{CHR}^2-\text{CO}-$) monomers linked *via* amide bonds (peptide bonds) [1]. Natural silk is a biopolymer that composed mainly of fibroin and is produced by certain insect larvae to form cocoons. Primary structure of fibroin protein mainly consists of the recurrent amino acid sequence $(\text{Gly-Ser-Gly-Ala-Gly-Ala})_n$ (Scheme 1) [2]. Due to the structurally ordered amino acid chains in the fibroin, silk proteins can form functional complexes with metals; therefore, silk protein-based materials have found application as solid supports for the immobilization of catalysts.

Catalytic oxidation processes play an important role in green organic transformations. The development of new catalytic materials based on green principles is of significant importance in organic chemistry. From both industrially and environmentally viewpoints, there is an important demand for greener approaches that employs aerobic catalytic oxidation processes with minimum amount of waste [3]. For this reason, various natural biopolymers have been employed as the solid support to produce green

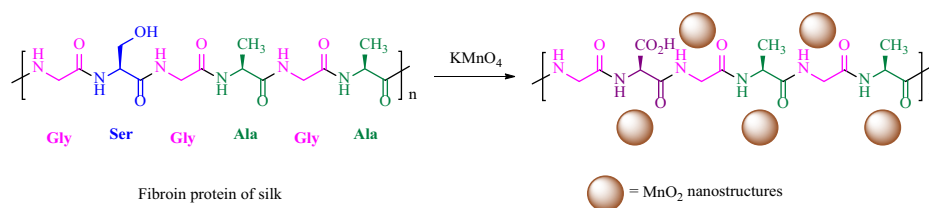
heterogeneous catalytic systems, such as cellulose [4], wool [5], alginate [6], gelatin [7], starch [8], and chitosan [9] derivatives. Among several renewable bio-supports, silk have unique properties and can be used as support for catalytic applications.

Manganese dioxide (MnO_2), as a cheap, renewable, mild, easily handled, and low toxic reagent, is one of the attractive materials due to its selective catalytic properties. MnO_2 has been extensively used as a selective catalyst for the oxidation of a variety of functional groups [3,10,11]. Unfortunately, MnO_2 usually has a relatively low surface area ($10\text{--}80\text{ m}^2\text{ g}^{-1}$) because of its aggregation into less active large particles during the reaction. Since aggregation of the heterogeneous catalysts substantially affected and decreased their catalytic activity, to settle the matter, nanostructured manganese dioxide was prepared for providing a catalyst with a large surface area. Moreover, aggregation of MnO_2 nanostructures is prevented by its distribution on the supports and high catalytic activity is accessible [12]. In addition, industrial applications of MnO_2 have become more attractive environmentally by the recycling of MnO_2 . For this reason, in our previous works it was suggested that it possible to separate the MnO_2 from a cellulose and wool biosupports by burning or chemical decomposition of biosupport [13,14].

As part of our ongoing program related to the developing new heterogeneous catalysts for organic transformations [15–18], and based on our previous investigations on MnO_2 [13,14,19–21], herein we report the synthesis of MnO_2 nanostructures on silk (MnO_2 @silk) and investigated its catalytic activities in the selective

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Scheme 1. Structure of fibroin protein of silk and the possible structure of MnO₂@silk.

aerobic oxidation of various of benzylic hydrocarbons, alcohols, and oximes into the corresponding aldehydes and ketones, and one-pot oxidative two-component reaction of aromatic hydrocarbons of petroleum naphtha in the absence of any other oxidizing reagent or initiator. We found the MnO₂ nanostructures are effectively immobilized on the surface of silk protein and prevented from its aggregation. In addition, there is the possibility of separation MnO₂ from silk support at the end of the catalytic process (Scheme 1).

2. Materials and methods

2.1. General

Natural white silk (silkworm cocoons of Gilan/Iran) was washed with NaOH solution, distilled water, and acetone, then cut with scissors to very short pieces (about 200 μm–1 mm, based on SEM images). All reagents were obtained from Aldrich or Merck and used without further purification. The elemental analyses were performed with an Elementar Analysensysteme GmbH VarioEL. X-ray diffraction (XRD) pattern of catalyst was recorded on a STOE STADI P with scintillation detector, secondary monochromator using Cu K α radiation ($\lambda = 0.1540$ nm). Mn(IV) determination was carried out on an FAAS (Shimadzu model AA-680 flame atomic absorption spectrometer) with a Mn hollow cathode lamp at 279.5 nm, using an air-acetylene flame. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of 10 °C min⁻¹ in air. Scanning electron microscopy (SEM) observations were carried out on an electron microscopy Philips XL-30 ESEM. All samples were sputtered with gold before observation. Products were analyzed using a Varian 3900 GC. Melting points were measured on an Electrothermal 9200 apparatus.

3. Experimental

3.1. Synthesis of MnO₂@silk

Natural white silk (silkworm cocoons of Gilan/Iran) was washed with NaOH solution (0.01 M), distilled water and acetone and dried at 60 °C, then cut with scissors to very short pieces (about 200 μm–1 mm, based on SEM images). For the synthesis of MnO₂@silk, a solution of KMnO₄ (0.01 M, 150 mL) was added dropwise to a magnetically stirred suspension of the natural silk pieces (1.0 g) in 200 mL of H₂O during 12 h at room temperature. The mixture was filtered to give brown MnO₂@silk. The prepared catalyst washed with H₂O (3 × 10 mL) and EtOH (3 × 10 mL), successively and dried under vacuum at 80 °C for 12 h.

3.2. Oxidation of alkyl arenes; General procedure

In a typical reaction, an alkyl arene (1.0 mmol), MnO₂@silk (0.09 g, 10 mol% of MnO₂), and *o*-xylene (5.0 mL) were added to a two-necked flask. The mixture was stirred under reflux conditions and air blowing. The thin layer chromatography (TLC) method was

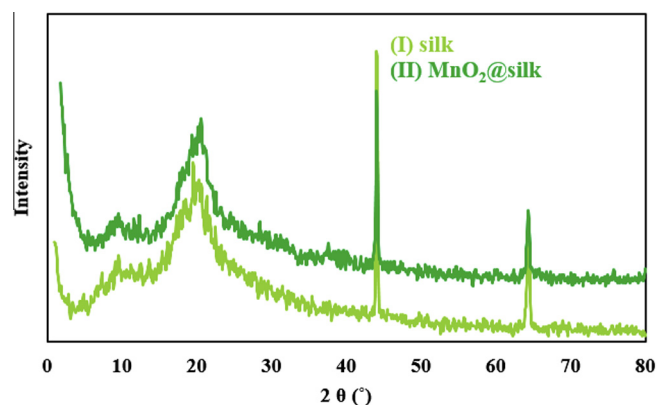


Fig. 1. XRD patterns of silk (I) and MnO₂@silk (II).

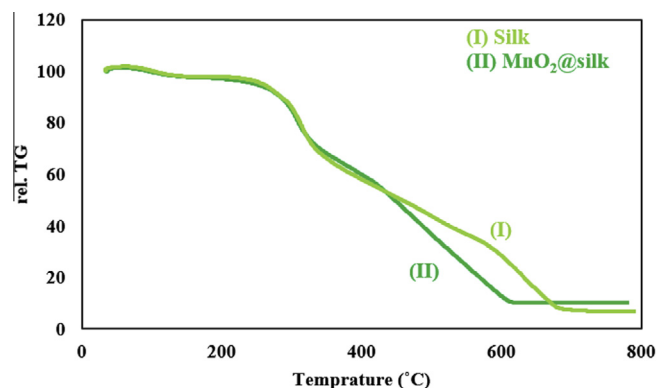


Fig. 2. TG curves of silk fibers (I) and MnO₂@silk (II) in air.

used to investigate the progress of the reaction. Upon completion, analysis of the crude product has been done by GC method.

3.3. Oxidation of alcohols; General procedure

In a typical reaction, an alcohol (1.0 mmol) was added to a two-necked flask containing MnO₂@silk (0.09 g, 10 mol% of MnO₂), K₂CO₃ (0.50 mmol), and *o*-xylene (5.0 mL) and stirred under air blowing at room temperature. The progress of the reaction was followed by TLC and GC method. After completion of reaction and filtration of mixture, the filtrate was analyzed by GC method.

3.4. Oxidation of oximes; General procedure

An oxime (1.0 mmol) and MnO₂@silk (0.09 g, 10 mol% of MnO₂) were well ground using a pestle at room temperature. The progress of the reaction was monitored by TLC and GC. After completion of the reaction, the solid was washed with dichloromethane. After the filtration of the reaction mixture, analysis of the filtrate has been done by GC method.

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