Ultrasonics Sonochemistry 17 (2010) 453–459

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Sonocatalytic epoxidation of alkenes by vanadium-containing polyphosphomolybdate immobilized on multi-wall carbon nanotubes

Hossein Salavati [a,*], Shahram Tangestaninejad [b], Majid Moghadam [b], Valiollah Mirkhani [b], Iraj Mohammadpoor-Baltork [b]

[a] *Department of Chemistry, Payame Noor University (PNU), 81395-671 Isfahan, Iran*
[b] *Department of Chemistry, Catalysis Division, University of Isfahan, 81746-73441 Isfahan, Iran*

ARTICLE INFO

Article history:
Received 21 May 2009
Received in revised form 10 September 2009
Accepted 25 September 2009
Available online 2 October 2009

Keywords:
Polyoxometalate
Alkene epoxidation
Multi-wall carbon nanotube
Ultrasonic irradiation

ABSTRACT

A Keggin type polyoxometalate (POM) has been immobilized in the unique network structure of multi-wall carbon nanotubes (CNTs). The vanadium-containing polyphosphomolybdate (PVMo) supported on CNTs, which was prepared by a one-step solid-state reaction, was characterized by FT-IR, XRD, SEM and elemental analyses. These uniform nanoparticles have an average size 20–30 nm. Furthermore, due to the chemical interaction between PVMo and carboxylic acid groups, PVMo nanoparticles were successfully immobilized on the CNTs. Moreover, the obtained composite was found as an efficient catalyst for oxidation of hydrocarbons under reflux and ultrasonic irradiation (US) conditions.

1. Introduction

Nanosystems, with characteristic lengths (1–100 nm), have become one of the most attractive subjects in materials science, chemistry, physics and biology. Therefore, the exploration of new nanostructure materials for various applications is still the first and one of the most significant challenges in nano science [2]. In the last decade, carbon nanotubes (CNTs) have attracted wide interest because of their unique physical properties and many potential applications such as one dimension quantum wires, optical switches, nano-transistors and other essential electronic components [1].

Polyoxometalates (POM) can also be practically used as solid catalysts if they could be physically immobilized on solid supports. Recently, Müller et al. have reported the synthesis of many POMs with nanometer size, including novel kinks, of large rings and wheel-shaped systems with 176 or even more Mo atoms [3]. In another work, the growing process of $[(NH_4)_3PW_{12}O_{40}]$ nanoparticles has been reported [4]. Due to the unique properties of POMs, the preparation of POMs nanocrystals and nano/micro-systems is of great interest [5]. Kang and co-workers reported the immobilization of POMs on carbon nanotube by direct synthesis of these molecules in the CNTs [6].

In this work, the chemical modification of CNTs by PVMo nanoparticles is reported. Based on the novel properties of both PVMo and CNTs, such structures may find a wide field of applications [6]. Recently, various efficient catalytic systems have been reported for epoxidation of alkenes with H_2O_2 using homogeneous or heterogeneous polyoxometalates as catalyst [7–12]. However, an important disadvantage associated with heterogeneous catalytic systems is their lower catalytic activity in comparison with homogeneous counterparts. In most cases the use of ultrasonic (US) wave (sonocatalysis) is recommended for solving this problem.

In general US has chemical and mechanical effects. The chemical effects of ultrasound do not derive from a direct coupling of the acoustic field with chemical species on a molecular level. Instead, sonochemistry and sonoluminescence derive principally from acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquids irradiated with high-intensity ultrasound. Bubble collapse during cavitation serves as an effective means of concentrating the diffuse energy of sound: compression of a gas generates heat. When the compression of bubbles occurs during cavitation, heating is more rapid than thermal transport, creating a short lived localized hot spot. There is a nearly universal consensus that this hot spot is the source of homogeneous sonochemistry [13,14].

* Corresponding author. Tel.: +98 311 7380003; fax: +98 311 7381002.
E-mail address: hosseinsalavati@pnu.ac.ir (H. Salavati).

1350-4177/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2009.09.011

The most successful applications of ultrasound have been found in the field of heterogeneous chemistry involving solids and metals. This is due to the mechanical impact of ultrasound on solid surfaces. In conventional chemistry there are several problems associated with reactions involving solids or metals: small surface area of the solid/metal may limit reactivity, penetration of reactants into deeper areas is not possible, oxide layers or impurities can cover the surface, reactants/products have to diffuse onto and from the surface and reaction products can act as deposit on the surface and prevent further reactions.

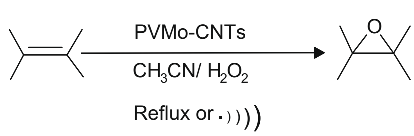
The mechanical effects of ultrasound offer an opportunity to overcome the following types of problem associated with conventional solid/metal reactions: break up of the surface structure allows penetration of reactants and/or release of materials from surface, degradation of large solid particles due to shear forces induced by shock waves and microstreaming leads to reduction of particle size and increase of surface area and accelerated motion of suspended particles leads to better mass transfer [15].

Recently, we reported the sonocatalytic oxidation of organic compounds catalyzed by vanadium-containing polyphosphomolybdate supported on MCM-41 and TiO_2 nanoparticles [7,8]. In this paper, we wish to report the sonocatalytic oxidation of alkenes with H_2O_2 catalyzed by $Na_5PV_2Mo_{10}O_{40}$ (PVMo) supported on multi-wall carbon nanotubes (CNTs). The effect of US irradiation on the catalytic activity of this catalyst was also investigated (Scheme 1).

2. Experimental

All chemicals were of analytical grade and were used without further purification. Elemental analysis was performed on a Perkin–Elmer 2400 instrument. Atomic absorption analysis was carried out on a Shimadzu 120 spectrophotometer. Diffuse reflectance spectra were recorded on a Shimadzu UV-265 instrument using optical grade $BaSO_4$ as reference. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with Nicolet-Impact 400D instrument. Scanning electron micrographs of the catalyst and support were taken on SEM Philips XL 30. Powder X-ray diffraction data were obtained on a D_8 Advanced Bruker using Cu Kα radiation (2θ = 5–70°). Gas chromatography experiments (GC) were performed on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. ^1H NMR spectra were recorded on a Bruker-Arance AQS 300 MHz. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification.

The $Na_5[PV_2Mo_{10}O_{40}]\cdot 14H_2O$ salt was prepared as described in the literature [16].



Scheme 1.

2.1. Preparation and characterization of PVMo–CNTs composite

The unmodified carbon nanotubes (multi-wall carbon nanotubes with diameters between 20 and 30 nm) were purchased from Shenzen NTP Factory and modified. Multi-wall carbon nanotubes containing carboxylic acid groups were the predominant groups expected to be acquired [17]. Subsequently, the CNTs were dispersed in *N,N*-dimethylformamine (DMF), yielding a black–brown suspension.

The typical preparation of PVMo/CNTs nanoparticles is as follows: PVMo (0.1 g) and CNTs (0.4 g) were put into an agate mortar and the surfactant Triton-X-100 (0.5 ml) was added drop-wise to the mixture. The mixture was thoroughly ground for 20 min, washed in a supersonic washing machine using absolute alcohol as dispersant, and centrifuged. The washing and centrifugalizing processes were repeated five times. The wet nanoparticles of PVMo–CNTs obtained and were dried in vacuum drying oven for 5 h (60–80 °C).

2.2. General procedure for oxidation reactions with H_2O_2 under reflux conditions

Reactions were carried out in a 50 ml thermostated glass reactor equipped with a magnetic stirrer. In a typical experiment, the reaction vessel was loaded with the supported catalysts (30 mg, containing 2.86 µmol of PVMo), alkene or alkane (0.8 mmol) in acetonitrile (5 ml). H_2O_2 (1 ml, 30%) was added and the mixture was refluxed. The progress of the reaction was monitored by GC. At the end of the reaction, the mixture was diluted with Et_2O

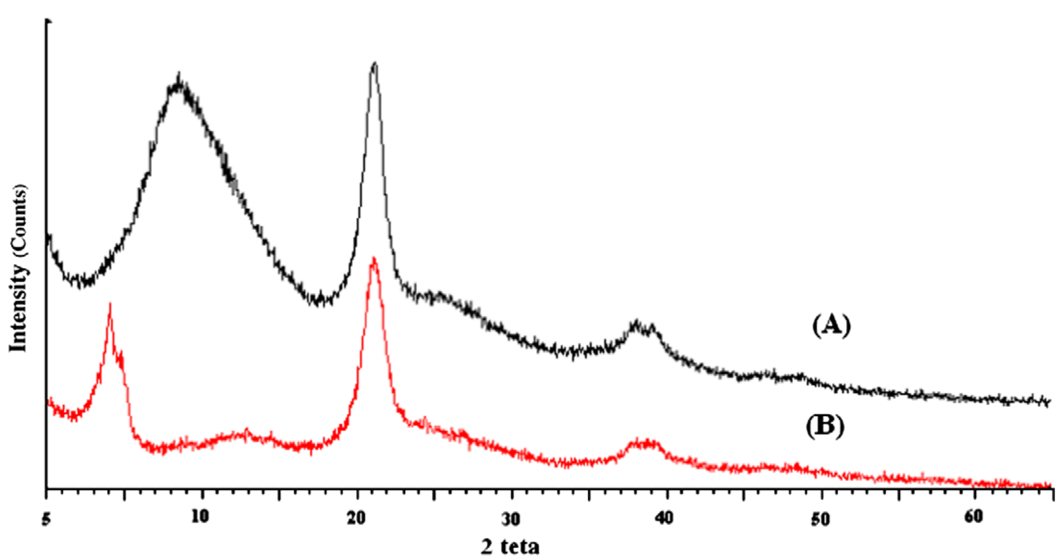


Fig. 1. XRD patterns of (A) CNTs and (B) PVMo–CNTs composite.