



Catalytic performance of a boron peroxotungstate complex under homogeneous and heterogeneous conditions

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ABSTRACT

The preparation and characterization (FT-IR, FT-Raman, ¹¹B MAS NMR, diffuse reflectance, elemental analysis) of a novel boron peroxotungstate (BTBA)₄H[BW₄O₂₄] (BTBA = benzyltributylammonium) is reported, along with its use in the homogeneous oxidation of *cis*-cyclooctene, geraniol, linalool and (–)-carveol with H₂O₂ as oxidant and acetonitrile as solvent. High catalytic activity was registered for all the substrates studied under homogeneous conditions, namely 99% of conversion of geraniol after 2 h, 93% for linalool after 5 h, 74% for *cis*-cyclooctene after 6 h, and 100% for (–)-carveol after 2 h of reaction. Some oxidation studies were carried out with the Venturello complex, [PW₄O₂₄]^{3–}, in the same conditions.

Furthermore, the boron peroxotungstate (BW₄) was immobilized using two different strategies: (a) BW₄ anchored into a functionalized silica (aptesSiO₂) giving BW₄@aptesSiO₂ and (b) BW₄ encapsulated on a metal organic framework, commonly referred as MIL-101, giving BW₄@MIL-101. The catalytic activity of both heterogeneous materials was investigated for geraniol oxidation and the results were compared with those obtained with BW₄ under homogeneous conditions. The encapsulated boron peroxotungstate (BW₄@MIL-101) gave rise to the best results, reaching complete conversion of geraniol after 3 h of reaction and 78% selectivity for 2,3-epoxygeraniol. Additionally, this heterogeneous catalyst could be reused without appreciable loss of catalytic activity, affording similar 2,3-epoxygeraniol selectivity. The heterogeneous catalysts' stability was also investigated after the oxidation reactions by different characterization techniques.

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1. Introduction

The transformation of natural compounds into valuable intermediates for organic synthesis is a significant line of study, both in the laboratory and in industry. In particular, the search for efficient and environmentally clean catalytic oxidative reactions has been much studied [1,2]. Among the oxidants available, the use of hydrogen peroxide (H₂O₂) in the catalytic oxidation of organic compounds has been gaining special attention since it is a safe, non-toxic, relatively low-cost reagent and easily manipulated after the reactions. Additionally, the only reduction product expected is water [3–6].

It is known that the reaction of hydrogen peroxide with certain metals (e.g. Mo^{VI}, W^{VI}, V^V) can yield peroxocomplexes, which are efficient oxidation catalysts in the presence of H₂O₂ [7,8], namely {(XO₄)[W(O)(O₂)₂]₄}^{3–}, the so-called Venturello peroxocomplex,

where X = P or As [9], and [M₂O₃(O₂)₄]^{2–}, where M = Mo, W [10,11]. Several groups have studied the Venturello peroxocomplexes or related systems [10–15]. Sergienko has reviewed the structures of almost all of the W and Mo peroxocomplexes known [16]. However, to our knowledge, no peroxotungsto- or peroxomolybdocomplex containing boron have been described.

All the tungsten peroxocomplexes mentioned above have been tested in the epoxidation of cyclic and linear alkenes with H₂O₂ under homogeneous conditions [8,11,17,18]. In the particular case of *cis*-cyclooctene oxidation with H₂O₂, this has already been studied using peroxocomplexes {(XO₄)[W(O)(O₂)₂]₄}^{3–}, where X = P or As, and [W₂O₃(O₂)₄]^{2–} as catalysts [10,11,19–21]. The studies reported so far under homogeneous conditions were carried out using chlorinated solvents or benzene as solvent, even though 100% selectivity to 1,2-epoxycyclooctane was always obtained, with no allylic oxidation products as by-products.

However, the oxidation of geraniol, linalool, carveol or other allylic alcohols with H₂O₂, catalysed by tungsten peroxocomplexes, has received much less attention [2,4,11,22–26]. To the best of our knowledge, the only reports for the catalytic oxidation of geraniol

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with H_2O_2 in a homogeneous medium is one where a cetylpyridinium salt of the Venturello complex is used in CHCl_3 [22] and our own work using tetrahexylammonium salt of $[\text{W}_2\text{O}_3(\text{O}_2)_4]^{2-}$ in CH_3CN [11]. Mizuno and co-workers used the dodecyltrimethylammonium salt of $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ in aqueous solution [23–26] in the same reaction. In all the previous cases, the main product formed is usually 2,3-epoxygeraniol. The oxidation of linalool was described using only the Venturello complex, giving rise to a mixture of the corresponding hydroxy furan and hydroxy pyran derivatives [22]. No reports on the oxidation of (–)-carveol with H_2O_2 in the presence of peroxocomplexes were found.

The immobilization of homogeneous catalysts on solid supports has attracted remarkable research interest since the resulting heterogeneous catalysts have the advantages of being easier to recover and to recycle. Some reports concerning the immobilization of peroxotungstates are known, employing inorganic materials such as Ti-silicalites or layered double hydroxides (LDHs) as supports [27,28]. Anion exchange of W compounds is another option, since most of the peroxocomplex catalysts are anionic in their active form [29]. Recently, some work has been done in the immobilization of peroxocomplexes via ionic liquid-modified silica [25,30,31].

In the present work, we present a new boron peroxotungstate ($\text{BTBA})_4\text{H}[\text{BW}_4\text{O}_{24}]$ (BTBA = benzyltributylammonium) and its use in the homogeneous oxidation of *cis*-cyclooctene, and some terpenic alcohols with two double bonds (geraniol, linalool and carveol) with H_2O_2 as oxidant and acetonitrile as solvent. For comparison, linalyl acetate was also oxidized in the same conditions. The boron peroxotungstate was immobilized using two different strategies, namely anchored on a functionalized silica material and encapsulated on a metal organic framework (MOF) commonly referred as MIL-101 [32–35]. The heterogeneous catalytic activity of these materials in the oxidation of geraniol was also determined and compared with the homogeneous performance in similar conditions.

2. Experimental

2.1. Reagents and methods

Hydrogen peroxide (30 wt.% solution in water) was purchased from Riedel-de-Haën, whereas *cis*-cyclooctene, geraniol, linalool, and (–)-carveol were purchased from Sigma–Aldrich. All other chemicals and solvents were used as received or distilled and dried using standard procedures. Silica with surface area of 590–690 m^2/g was used as received from Sigma–Aldrich.

Elemental analyses for W and B were performed by ICP spectrometry (University of Aveiro, Central Laboratory of Analysis) and C, H, N elemental analyses were performed on a Leco CHNS-932 apparatus. Weight loss was determined by thermogravimetric analysis performed between 30 and 700 °C at 5 °C/min on a TGA-50 Shimadzu thermobalance. Infrared absorption spectra were recorded on a Mattson 7000 FTIR spectrometer, using KBr pellets. Raman spectra were measured using a Brüker RFS100/s FT-Raman spectrometer (Nd:YAG laser 1064 nm excitation). Powder X-ray diffraction (XRD) was performed on powders deposited on silicon substrates, using a Philips X'Pert instrument operating with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 40 kV/50 mA. ^{11}B MAS NMR spectra were recorded with a Bruker Avance 400 spectrometer at 128.37 MHz, using spinning rates of 14 kHz. The ^{11}B MAS NMR spectra were recorded with 15° pulses and 5 s recycle delays. Chemical shifts are quoted in ppm from $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. Matrix Assisted Laser Desorption Ionization (MALDI) mass spectra (MS) were acquired, in positive mode, with a MALDI-TOF/TOF Applied Biosystems 4800 Proteomics Analyser (Applied Biosystems, Framingham, MA, USA) instrument equipped with a nitrogen laser emitting

at 337 nm and operating in a reflectron mode. MALDI-MS spectra were acquired using α -cyano-hydroxycinnamic acid (Aldrich), prepared in acetonitrile/(water:trifluoroacetic acid 0.1%) 50/50 as matrix. The GC–MS analyses were performed on a Finnigan Trace GC–MS (Thermo Quest CE instruments) using helium as the carrier gas (35 cm/s); GC-FID analyses were performed using a Varian Star 3900 chromatograph and helium as the carrier gas (35 cm/s). Fused silica capillary columns of the DB-5 type (30 m \times 0.25 mm i.d.; 25 μm film thickness) were used, in both cases.

2.2. Synthesis of the catalysts

$(\text{C}_{19}\text{H}_{34}\text{N})_4\text{HBW}_4\text{O}_{24}$ [BW_4]. 12 mL of 30 wt.% H_2O_2 were added to an aqueous solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (10 mmol, 20 mL). The pH of the resulting solution was adjusted with HCl 6 M until the obtainment of a colourless solution (pH = 2.8). To the resulting solution, H_3BO_3 in water (0.26 M, 10 mL) was added dropwise, with stirring during 30 min. Finally, an aqueous solution of benzyltributylammonium chloride (BTBACl , 20 mmol, 10 mL) was added. A white solid was obtained and then filtered, washed and dried in a desiccator under vacuum. Yield, 88%. Anal. found (%): W, 33.4; B, 0.48; C, 40.0; H, 6.62, N, 2.53. Calcd (%): W, 32.9; B, 0.48; C, 40.8; H, 6.13, N, 2.50. Total weight loss found: 56.8%; calcd: 55.9%. FT-IR (cm^{-1}): 954, 868, 840, 727, 703, 640, 569. FT-Raman (cm^{-1}): 1006, 964, 912, 852, 622, 566, 335, 302, 258. MALDI-MS: 2236.4 Da, corresponding to the expected formula $(\text{C}_{19}\text{H}_{34}\text{N})_4\text{HBW}_4\text{O}_{24}$.

$(\text{C}_{24}\text{H}_{52}\text{N})_3\text{PW}_4\text{O}_{24}$ [PW_4]. This compound was prepared by an adaptation of a described procedure [10,36]. A solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (3.76 g, 10.0 mmol) in water (15 mL) and 30% H_2O_2 (7 mL) was heated for 4 h at 60 °C, giving a colourless solution. Then an aqueous solution of Na_2HPO_4 (0.36 g; 2.5 mmol in 5 mL of H_2O) was added. After cooling the solution to room temperature, a solution of $[\text{N}(\text{C}_6\text{H}_{13})_3]\text{Cl}$ (1.56 g, 4.0 mmol) in toluene (40 mL) was added dropwise. The results obtained for the characterization of this compound are in agreement with those previously published [10,36].

MIL-101. This solid support was prepared by the adaptation of the original method reported by Férey et al. [32]. A mixture containing chromium(III) nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2 mmol], 1,4-benzenedicarboxylic acid (H_2bdc , 2 mmol) and hydrofluoric acid (100 μL) in H_2O was stirred at room temperature. The resulting suspension was transferred to an autoclave and heated at 493 K for 9 h. After cooling, a significant amount of H_2bdc (as crystals) was observed with the desired material (green thin powder). The purification of the MIL-101 material was performed by a double DMF treatment, followed by a double treatment in ethanol. FT-IR (cm^{-1}): 3465, 1670, 1621, 1508, 1403, 1018, 748, 665, 588, 387. FT-Raman (cm^{-1}): 3074, 2935, 1611, 1458, 1146, 1040, 872, 812, 632.

Immobilization of BW_4 . Composite materials based on BW_4 were prepared by its immobilization in two different solid supports: silica (SiO_2) and metal-organic framework (MIL-101):

$\text{BW}_4@\text{aptesSiO}_2$. To immobilize BW_4 on SiO_2 , the surface of SiO_2 was initially modified by the grafting methodology, adapted from the literature [37]. The dried SiO_2 (1 g) was refluxed for 24 h in dry toluene (30 mL) with 3 mmol of 3-aminopropyltriethoxysilane (aptes) under argon. The functionalized support aptesSiO_2 was then treated with nitric acid to protonate the amine groups on the surface of the material. The protonated material is subsequently washed, filtered and dried. The immobilization of the boron peroxotungstate was performed by stirring the mixture of treated 0.3 g of treated aptesSiO_2 in 20 mL of acetonitrile with 30 mg BW_4 for 24 h at room temperature. The resulting solid was filtered, washed with acetonitrile and dried at room temperature. Anal. found (%): W, 4.25; B, 0.06; Si, 30.6; loading of boron peroxotungstate: 0.058 mmol per 1 g.

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