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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, ^{11}B MAS NMR, diffuse reflectance, elemental analysis) of a novel boron peroxotungstate $(BTBA)_4H[BW_4O_{24}]$ (BTBA = benzyltributylammonium) is reported, along with its use in the homogeneous oxidation of *cis*-cyclooctene, geraniol, linalool and (−)-carveol with H_2O_2 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, $[PW_4O_{24}]^{3-}$, in the same conditions.

Furthermore, the boron peroxotungstate (BW_4) was immobilized using two different strategies: (a) BW_4 anchored into a functionalized silica (aptesSiO_2) giving BW_4@aptesSiO_2 and (b) BW_4 encapsulated on a metal organic framework, commonly referred as MIL-101, giving BW_4@MIL-101. The catalytic activity of both heterogeneous materials was investigated for geraniol oxidation and the results were compared with those obtained with BW_4 under homogeneous conditions. The encapsulated boron peroxotungstate (BW_4@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 (H_2O_2) 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 H_2O_2 [7,8], namely $\{(XO_4)[W(O)(O_2)_2]_4\}^{3-}$, the so-called Venturello peroxocomplex, where X = P or As [9], and $[M_2O_3(O_2)_4]^{2-}$, 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 H_2O_2 under homogeneous conditions [8,11,17,18]. In the particular case of *cis*-cyclooctene oxidation with H_2O_2, this has already been studied using peroxocomplexes $\{(XO_4)[W(O)(O_2)_2]_4\}^{3-}$, where X = P or As, and $[W_2O_3(O_2)_4]^{2-}$ 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 H_2O_2, 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 $[W_2O_3(O_2)_4]^{2-}$ in CH_3CN [11]. Mizuno and co-workers used the dodecyltrimethylammonium salt of $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ 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 $(BTBA)_4H[BW_4O_{24}]$ (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 Cu-K_α radiation ($\lambda = 1.54178$ Å) 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 $BF_3{\cdot}O(C_2H_5)_2$. 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 × 0.25 mm i.d.; 25 μm film thickness) were used, in both cases.

2.2. Synthesis of the catalysts

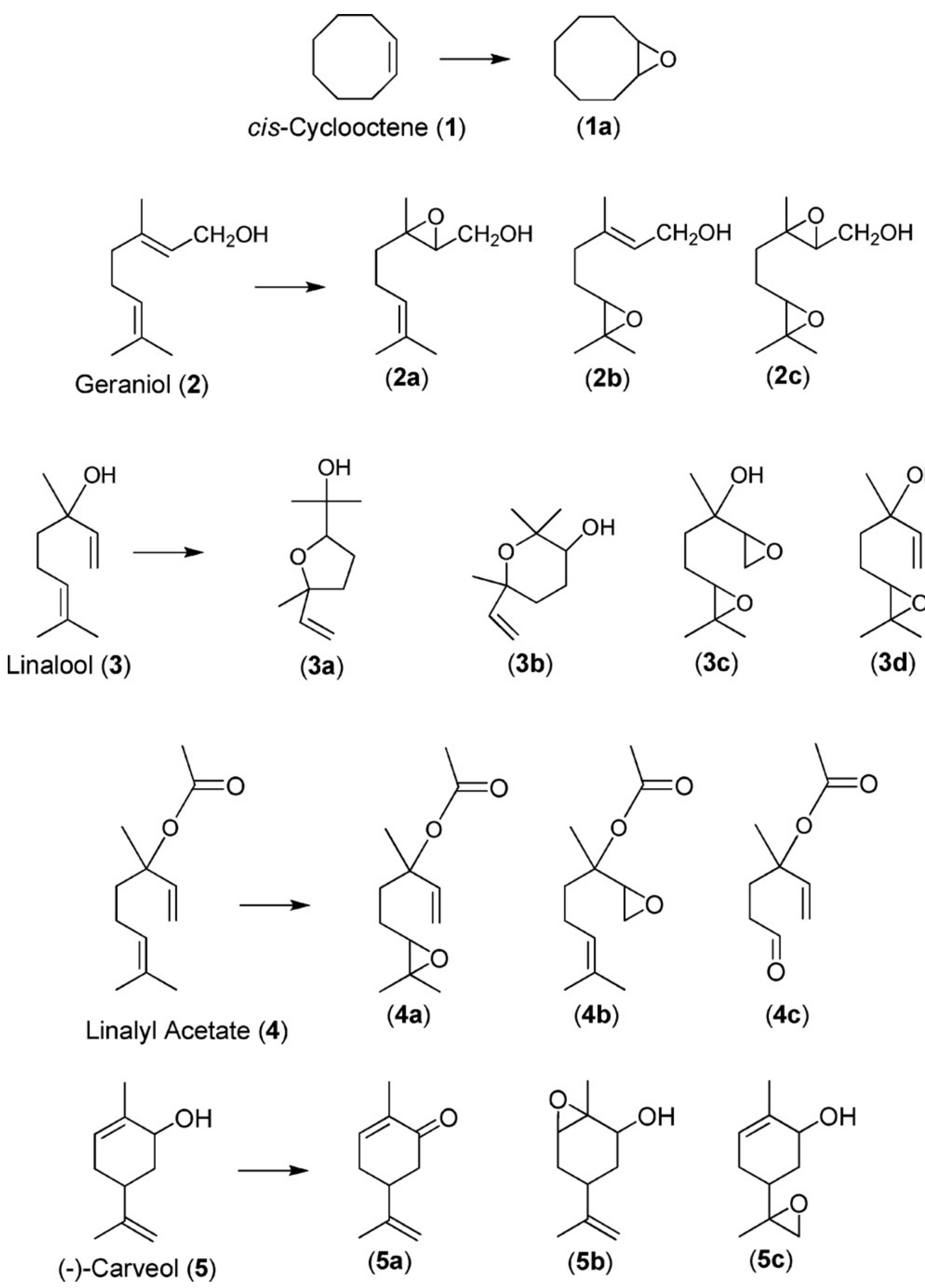
$(C_{19}H_{34}N)_4HBW_4O_{24}$ [BW_4]. 12 mL of 30 wt.% H_2O_2 were added to an aqueous solution of $Na_2WO_4{\cdot}2H_2O$ (10 mmol, 20 mL). The pH of the resulting solution was adjusted with HCl 6 M until the obtainment of a colourless solution (pH = 2.8). To the resulting solution, H_3BO_3 in water (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 $(C_{19}H_{34}N)_4HBW_4O_{24}$.

$(C_{24}H_{52}N)_3PW_4O_{24}$ [PW_4]. This compound was prepared by an adaptation of a described procedure [10,36]. A solution of $Na_2WO_4{\cdot}2H_2O$ (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 $[N(C_6H_{13})]Cl$ (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 [$Cr(NO_3)_3{\cdot}9H_2O$, 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):

BW_4@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.



Scheme 1.

BW_4@MIL-101. The encapsulation of BW_4 in MIL-101 was performed by adapting a published procedure [38]. Initially, an acetonitrile solution of 10 mM of BW_4 (50 mL) was prepared and then 0.5 g of MIL-101 was added and stirred for 24 h at room temperature. After that, the solid was filtrated and washed several times with acetonitrile. Anal. found (%): W, 12.11; B, 0.17; loading of boron peroxotungstate: 0.165 mmol per 1 g; FT-IR (cm^{-1}): 3436, 1670, 1619, 1509, 1401, 1018, 954, 840, 750, 665, 582, 385. FT-Raman (cm^{-1}): 3072, 2931, 1613, 1455, 1144, 1006, 964, 872, 809, 635.

2.3. Oxidation reaction procedure

The oxidation reactions of *cis*-cyclooctene (**1**), geraniol (**2**), linalool (**3**), linalyl acetate (**4**) and (−)-carveol (**5**) (Scheme 1) were carried out in acetonitrile, in a closed 5 mL reaction vessel equipped with a magnetic stirrer, using H_2O_2 (30 wt.%) as oxidant. The oxidation reactions of **1**, **3**, **4** and **5** were performed at 80 °C whereas the oxidation reactions of **2** were done at room temperature and protected from light. The homogeneous reactions were typically carried out as follows: the substrate and the required amount of catalyst were dissolved in acetonitrile (1.5 mL) and stirred; then the required amount of 30% (w/w) aqueous H_2O_2 was added to the reaction mixture. Aliquots were taken directly from the reaction mixture and injected into the GC-FID or GC–MS equipments for analysis of the starting materials and products. Similar conditions were used in heterogeneous reactions. The studies in heterogeneous conditions were performed only with geraniol (**2**). The amount of catalyst used was 20 mg for BW_4@MIL-101 and 40 mg for BW_4@aptesSiO$_2$ and the aliquots were centrifuged and then injected into the GC-FID or GC–MS equipments. At the end of the reactions the heterogeneous catalysts were separated from the reaction mixtures by centrifugation and washed with different solvents (CH_3CN and C_2H_5OH) to remove the remaining substrate and oxidant, as well as the reaction products. The recovered catalysts were dried under vacuum at room temperature and used in a new reaction under identical experimental conditions, with readjustment of all quantities, without changing the molar ratios and reaction concentrations. The reaction products reported here were identified as described elsewhere [11,39,40]. In the case of linalool and (−)-carveol oxidation, the reaction products were identified by comparison to the GC–MS library. Blank reactions were performed for all substrates, confirming that no oxidation products are obtained unless the catalyst and H_2O_2 are both present. Even in the presence of the supports (aptesSiO_2 or MIL-101) and H_2O_2 no oxidation products were obtained. Acetamide was never observed among the reaction products. Thus, the possibility of formation of peroxyimidic acid, which would function as the oxidizing agent, was excluded.

3. Results and discussion

3.1. Synthesis and characterization of $(C_{19}H_{34}N)_4HBW_4O_{24}$ [BW_4]

Dimeric oxo-bridged peroxotungstates containing $WO(O_2)_2$ units are formed in aqueous solutions of sodium tungstate and H_2O_2 with the decreasing of pH [36,41]. In the presence of some oxoacids (e.g. H_3PO_4, H_3AsO_4), the products can incorporate the central element of that acid, giving rise to species containing one or more than one $WO(O_2)_2$ units linked to a XO_n group, like the PO_4 in the Venturello complex, $\{(PO_4)[WO(O_2)_2]_4\}^{3-}$ (or $[PW_4O_{24}]^{3-}$) [36]. Besides the choice of the oxoacid and the pH in solution, another important factor influencing the isolation of the peroxocomplexes is the countercation chosen. So far, no peroxocomplexes that incorporate boron in its structure had been reported. In a previous study it was found that the dimeric species $[W_2(O)_3(O_2)_4]^{2-}$ was precipitated from solutions obtained by mixing aqueous solutions of $Na_2WO_4{\cdot}2H_2O$ and 30% H_2O_2 with pH adjustment to 2.8, followed by the addition of boric acid, and of tetrahexylammonium chloride [11]. In the present work we have used the same methodology of Ref. [11], but using benzyltributylammonium chloride. The white solid obtained was analysed by infrared, Raman and ^{11}B solid-state NMR spectroscopy, elemental and thermogravimetric analyses and all the data are in accordance with a new peroxocomplex with the following general formulae $(C_{19}H_{34}N)_4HBW_4O_{24}$. The mass analysis (MALDI-MS) for BW_4 gave the expected ion $[M]^+ = 2236.4$ Da, which is also consistent with the formula given above.

The presence of boron was confirmed by elemental analysis and ^{11}B solid MAS NMR spectroscopy (Fig. 1). It is possible to observe a second-order quadrupole powder pattern, which was simulated yielding an isotropic chemical shift, $\delta_{iso} = 10.4$ ppm, and a quadrupole coupling constant $C_Q = 1.201$ MHz. These results show that boron is in a relatively distorted BO_4 environment [42,43].

The peroxocomplexes have characteristic FT-IR spectra, presenting bands in the range of 500–650 cm^{-1}, attributable to asymmetric and symmetric vibrations of the peroxo bonds $[W(O_2)]$ [12,13]. BW_4 shows the peroxo $W(O_2)$ bands at 590 and 640 cm^{-1} (Fig. 2). It is also possible to observe the W═O and O–O vibrations at 954 and 868, 840 cm^{-1}, respectively. The characteristic band of the ν(B–O), in polyoxometalate anions, is usually overlapped with the $\nu(W{-}O_b{-}W)$ vibration, and this band typically appears near 920 cm^{-1} [44]. BW_4 shows a weak band at 921 cm^{-1}, that is likely to be attributed to the ν(B–O) vibration. The FT-Raman spectrum of BW_4 (Fig. 3) confirms the presence of the peroxo bond $[W(O_2)]$ at 622 and 566 cm^{-1}, and the W═O and O–O vibrations are also evident at 964 and 852 cm^{-1}, respectively. The ν(B–O) vibration appears at 912 cm^{-1}, which is in agreement with the literature data for this bands [45].

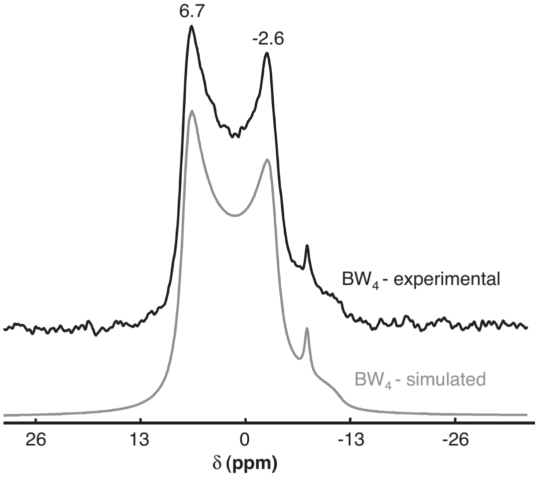


Fig. 1. ^{11}B MAS NMR spectrum of solid compound BW_4 (experimental – top and simulated – bottom). The signal of weak intensity at −7.6 ppm may be due to the existence of an impurity, most likely from $BW_{12}O_{40}$.

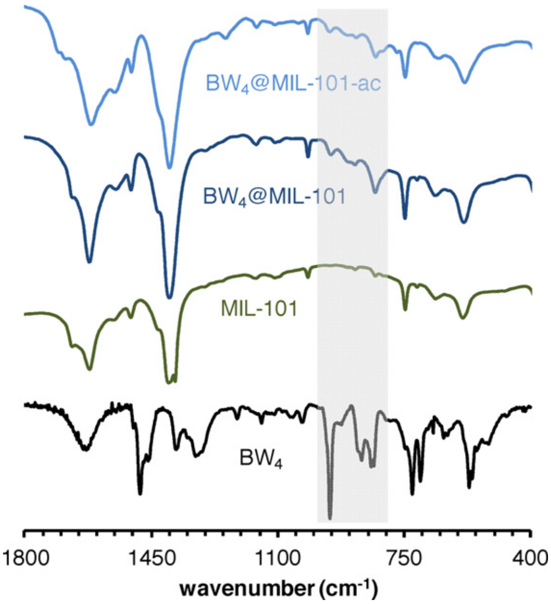


Fig. 2. FT-IR spectra of BW_4, MIL-101, BW_4@MIL-101 and BW_4@MIL-101-ac, in the wavenumber region between 400 and 1800 cm^{-1} (ac = after catalysis).

It was not possible to obtain single crystals of BW_4, in order to identify the structure of the new compound synthesized. The corresponding powder X-ray diffractogram shows the high crystallinity of the sample, since most of the observed peaks are well defined and have high intensity, as shown in Fig. 4. However, the identification was not possible by comparison of the XRD pattern with the indexed ones in the database [46].

3.2. Synthesis and characterization of the supported catalysts

The peroxotungstate BW_4 was immobilized following two different strategies: (i) immobilization on a silica support functionalized with 3-aminopropyltriethoxysilane (BW_4@aptesSiO_2); (ii) encapsulation of BW_4 into the nanocages of a metal-organic-framework MIL-101 (BW_4@MIL-101). From the elemental analyses it is possible to determine average loadings of 0.058 and

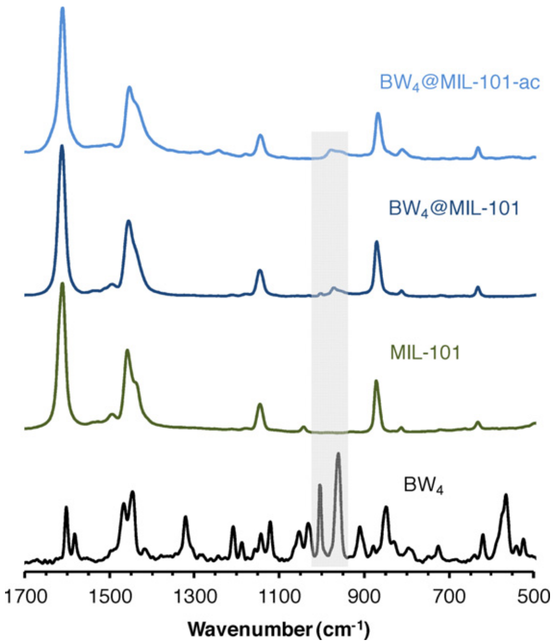


Fig. 3. FT-Raman spectra of BW_4, MIL-101, BW_4@MIL-101 and BW_4@MIL-101-ac, in the wavenumber region between 500 and 1700 cm^{-1} (ac = after catalysis).

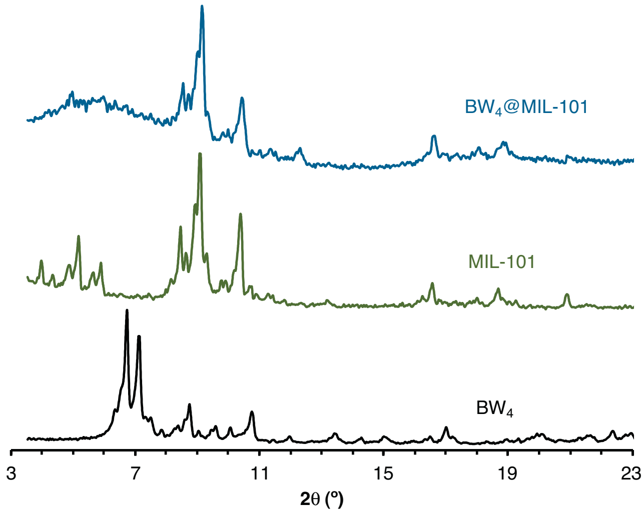


Fig. 4. Powder X-ray diffraction patterns for BW_4, MIL-101 and BW_4@MIL-101.

0.165 mmol per 1 g of material, respectively. In the case of the immobilization onto the silica support the peroxocomplex is probably supported by electrostatic interactions with the ammonium groups. In the case of the MOF support the peroxocomplex appears to be encapsulated.

In order to verify that the active peroxo species BW_4 remain intact after the immobilization into the supports, vibrational spectra were recorded (FT-IR and FT-Raman spectra). In the case of BW_4@aptesSiO_2 both of these techniques were not able to provide good information as the vibrations of the supporting material interfered with the typical peroxo vibrations. Fig. 2 shows the FT-IR spectra of the peroxocomplex, of the MIL-101 and of the supported material BW_4@MIL-101, in the wavenumber region between 400 and 1800 cm^{-1}. When comparing the three spectra it is possible to find, in the BW_4@MIL-101 material, all the bands of the support and also two extra small bands near 954 and 840 cm^{-1}, which were attributed to the W=O and O–O vibrations, respectively, in the BW_4 peroxocomplex.

Fig. 3 confirms the presence of BW_4 in this material. In the BW_4@MIL-101 FT-Raman spectrum it is possible to observe the presence of the support and the two small bands near 1006 and 964 cm^{-1} can be attributed to the BW_4 peroxocomplex. These results, together with the FT-IR data and the elemental analysis, suggest that the encapsulation of the BW4 into the MIL-101 support was effective.

The powder XRD pattern of the material BW_4@MIL-101 (Fig. 4, top) indicates that the crystalline structure of the solid support was retained after the encapsulation of the peroxo complex, since the main diffraction peaks are maintained unchanged. As expected, the crystalline structure of BW_4 is completely transformed during the insertion into the MIL-101, since no diffraction peaks of the complex are visible in the diffractogram of BW4@MIL-101. This observation confirms that all the peroxo complex present in the material are in non-crystalline form, most probably due to encapsulation in the MIL-101 cavities.

3.3. *Homogeneous catalysis*

The oxidation of *cis*-cyclooctene (**1**), geraniol (**2**), linalool (**3**), linalyl acetate (**4**) and (−)-carveol (**5**) (Scheme 1 and Table 1) with H_2O_2 were performed in the presence of catalytic amounts of the peroxocomplexes BW_4 and PW_4, using acetonitrile as solvent. These substrates (except **4**) were chosen to evaluate the catalytic activity of the new peroxocomplex BW_4 towards the epoxidation of an alkene and allylic alcohols with hydrogen peroxide, given that peroxocomplexes are known as good epoxidation catalysts. Under the conditions used, *cis*-cyclooctene gives only the corresponding epoxide (**1a**), geraniol gives mainly the 2,3-epoxide (**2a**), linalool affords predominantly the furan hydroxyl ether (**3a**), the 6,7-epoxide (**4a**) is the main product for linalyl acetate oxidation and (−)-carveol affords carvone (**5a**) and 2,3-epoxide (**5b**) as the major products (Scheme 1). For comparison, the Venturello complex, $(C_{24}H_{52}N)_3PW_4O_{24}$, was used in similar conditions.

The first stage on the catalytic studies was to evaluate the oxidation reaction of *cis*-cyclooctene (**1**, Scheme 1), as a model substrate. The conversion of *cis*-cyclooctene in the presence of BW_4 reached 76% after 6 h of reaction at 80 °C, achieving only the 1,2-epoxycyclooctane, corresponding to a turnover number (TON) of 456 (Table 1). This result is less interesting than that obtained with $[W_2O_3(O_2)_4]^{2-}$ in similar conditions [11].

Geraniol (**2**, Scheme 1), linalool (**3**, Scheme 1) and carveol (**5**, Scheme 1) are allylic alcohols that offer several possible places of oxidative attack, namely at the two double bonds. These three different alcohols allow us to evaluate how the position of the hydroxy group can influence the outcome of the oxidation reactions.

The oxidation of geraniol took place at room temperature. The GC analyses of the reaction mixtures (Table 1) show that 2,3-epoxygeraniol (**2a**) was the main product, with selectivity between 76% and 90% depending on the amount of H_2O_2 used and reaction time, and conversion always above 95%. Two other unidentified products were obtained, possibly cyclic derivatives [47], together with a small amount of diepoxide. For the higher conversion, 330 TON and 1022 TOF (h^{-1}, determined after 10 min) were obtained, after 2 h of reaction.

The regioisomeric product distribution seems to be dominated by the relative electron density of the two double bonds, that favours epoxidation of geraniol at the C_6–C_7 position [22,40], because electron density at C_2–C_3 double bond is significantly depleted by the inductively electron-accepting hydroxyl group [22]. When preferential epoxidation at the C_2–C_3 position has been found, a complex involving the metal centre, the oxidant and the substrate, that may coordinate through the OH group might be implicated [22,48,49]. Since 2,3-epoxygeraniol was obtained as the

Table 1
Homogeneous epoxidation of the several substrates with H_2O_2 in the presence of the peroxocomplexes.

Substrate	Catalyst	Sub:H_2O_2	Time (h)	Conversion (%)[a]	TON[b]	Products selectivity (%)[a]			
cis-Cyclooctene[c]						**1a**			
	BW_4	3:3	6	76	456	100			
	PW_4	3:3	6	74	444	100			
Geraniol[d]						**2a**	**2b**	**2c**	
	BW_4	1:1	5	95	316	90	0	1	
	BW_4	1:2	3	96	320	89	0	1	
	BW_4	1:4.5	2	99	330	76	0	2	
	PW_4	1:4.5	2	95	316	70	16	3	
Linalool[e]						**3a**	**3b**	**3c**	**3d**
	BW_4	1:2	5	93	310	59	17	23	1
	PW_4	1:2	5	82	273	63	18	0	19
Linalyl Acetate[e]						**4a**	**4b**	**4c**	
	BW_4	1:2	6	84	280	90	9	1	
	PW_4	1:2	6	86	286	78	19	3	
Carveol[e]						**5a**	**5b**	**5c**	
	BW_4	1:2	2	100	333	56	37	1	
	PW_4	1:2	2	100	333	52	24	20	

[a] Determined by gas chromatography.
[b] mol of total products/mol of catalyst used.
[c] Reaction conditions: catalyst 5 μmol; CH_3CN (1.5 mL); *cis*-cyclooctene 3 mmol; H_2O_2 30% 3 mmol; 80 °C.
[d] Reaction conditions: catalyst 3 μmol; CH_3CN (1.5 mL); geraniol 1 mmol; H_2O_2 30% 4.5 mmol; room temperature and protected from light.
[e] Reaction conditions: catalyst 3 μmol; CH_3CN (1.5 mL); substrate 1 mmol; H_2O_2 30% 2 mmol; 80 °C.

main product, in the presence of the new peroxocomplex BW_4, the presence of such intermediate may be suggested.

The oxidative reactions of linalool (**3**, Scheme 1) were carried at 80 °C. In this case, the favoured double bond was the C_6–C_7 position, since it is through the 6,7-epoxide that the hydroxy furan **3a** and hydroxy pyran **3b** are formed [22], indicating that in this case the OH group does not possibly influence the selectivity. So the main product obtained in the oxidation of linalool is **3a** (Table 1), with 59% of selectivity, after 5 h of reaction, and 93% of conversion (310 TON). In order to elucidate the mechanism of formation of **3a** via 6,7-epoxylinalool, the oxidation of linalyl acetate (**4**) was studied (Scheme 1). Also in this case the double bond at the C_6–C_7 position was favoured, affording mainly the 6,7-epoxide **4a**. The cyclization of **4a** cannot occur, due to the acetate group.

The oxidative reactions of (−)-carveol (**5**, Scheme 1) were carried at 80 °C. In this case, the oxidation products occurred with 100% conversion after 2 h and originated predominantly carvone (**5a**) and 2,3-epoxide (**5b**). As in the case of geraniol, the epoxidation at the double bond nearer to the hydroxyl group is preferred.

Many papers have described the use of peroxotungstate based catalysts for epoxidations of allylic and homoallylic alcohols with H_2O_2. The obtained products are, generally, those indicated in Scheme 1 but conversion and selectivities are much dependent on the reaction conditions, namely solvent, concentrations, and H_2O_2/substrate molar ratio. Mizuno et al. have presented and reviewed the results obtained in several papers [8,17,18,50]. In particular, hydroxy furan **3a** and hydroxy pyran **3b** were previously obtained in the presence of a peroxotungstophosphate plus hydrogen peroxide [22]. The results obtained for geraniol in Table 1 show that the increase in the H_2O_2/substrate molar ratio leads to higher conversion in a shorter time, but with lower selectivity. In identical conditions, the conversion and selectivity for **2a** are slightly higher in reactions with BW_4 than with PW_4.

The studies carried out with the Venturello complex, PW_4, in order to compare the catalytic performance of PW_4 and BW_4, were carried out in the conditions for which BW_4 had originated the higher conversion values. The results are presented in Table 1. It is possible to see that the obtained conversions for all the substrates were not very different, being equal or marginally higher for BW_4 than for PW_4 for the allylic alcohols. BW_4 or PW_4 give rise only to some differences in the selectivities, even though the main products are always the same. In particular, it may be noted that the yield of the 6,7-epoxy **2b** and **5c** seems to be higher in the presence of PW_4 than of BW_4, and that the yield of the diepoxy **3c** is significant for BW_4 but null for PW_4. As the outcome of the reaction may depend on several variables, no explanations for these facts were attempted. In spite of these differences, the behaviour of BW_4 and PW_4 are, overall, similar.

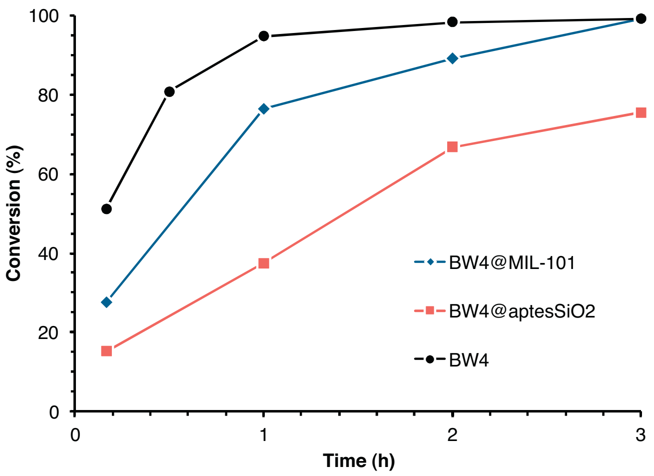


Fig. 5. Kinetic profiles for the oxidation of geraniol with H_2O_2 in the presence of homogeneous and heterogeneous catalysts.

3.4. Heterogeneous catalysis

Heterogeneous catalysts based on peroxotungstate BW_4 were tested for the reaction where homogeneous BW_4 presented higher catalytic performance, namely geraniol epoxidation. The reaction conditions were similar to that used for the homogeneous system. The catalytic performance of the two heterogeneous catalysts was investigated. Fig. 5 compares the kinetic profiles for the homogeneous BW_4 system and for the two heterogeneous catalysts: BW_4@aptesSiO_2 and BW_4@MIL-101. The main difference of

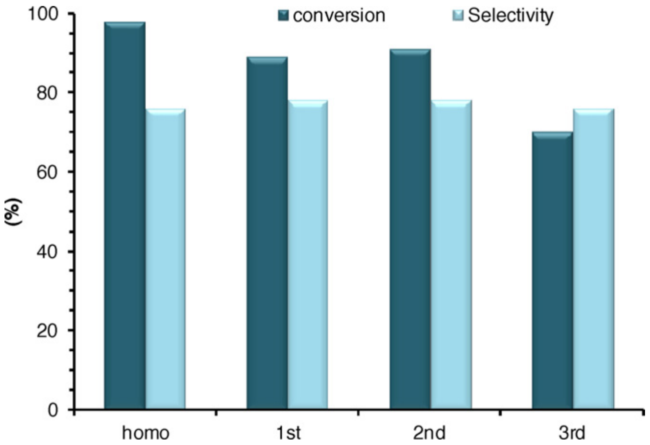


Fig. 6. Conversion and selectivity for 2,3-epoxygeraniol for the homogeneous system and different recycling cycles for the oxidation of geraniol after 2 h of reaction, for BW_4@MIL-101.

these two heterogeneous catalysts consists on the support where BW_4 was immobilized and also on the methodology of immobilization, which led to different loadings. In the homogeneous and heterogeneous systems the selectivity was similar and 2,3-epoxygeraniol (**2a**) was the main product (78 and 75% of selectivity with BW_4@MIL-101 and BW_4@aptesSiO$_2$, respectively). A slightly increase in yield for the main product was also observed with reaction time. A complete conversion of geraniol was observed for the homogeneous system after 2 h of reaction and the same was achieved in the presence of BW_4@MIL-101 after 3 h of reaction. At this time, the BW_4@aptesSiO$_2$ system gives 75% of conversion, in the conditions used. Turnover frequencies (TOF/h^{-1}) were calculated after 10 min of reaction and the higher result was obtained for BW_4 (1022 TOF), followed by the BW_4@MIL-101 (501 TOF) and the lower activity was found to BW_4@aptesSiO$_2$ (394 TOF).

The solid catalysts can be easily separated by filtration to be used in a new reaction under identical experimental conditions. The catalysts were recycled in order to test their stability and activity in consecutive reaction cycles. Fig. 6 illustrates the reusability of the heterogeneous system BW_4@MIL-101 for geraniol oxidation with H_2O_2 after 2 h of reaction. It can be seen that this catalyst is active for at least three consecutive cycles and almost complete conversion was found also for the second reaction cycle. Similar behaviour was observed for BW_4@aptesSiO$_2$ for the first two reaction cycles. The conversion obtained after 2 h of reaction is 65% for the first cycle, 56% for the second cycle and 25% for the third cycle. The selectivity for different cycles is analogous, showing a slightly increase during reaction time for the 2,3-epoxygeraniol.

The heterogeneous catalysts BW_4@MIL-101 and BW_4@aptesSiO$_2$ recovered after the three cycles were characterized by different techniques, in order to check their stability after reaction. The stability was confirmed by FT-IR and FT-Raman spectroscopy, where the characteristic bands can be observed [Fig. 2, BW_4@MIL-101-ac; Fig. 3, BW_4@MIL-101-ac], the pattern being the same before and after catalysis.

In order to further investigate the catalytic activity of the heterogeneous catalysts versus the putative homogeneous reaction after leaching of the active species from the support, the solid catalyst was separated from the reaction mixture by careful filtration after 10 min of reaction for BW_4@MIL-101 system and after 1 h for BW_4@aptesSiO2. These times were chosen taking into account that conversion should be higher than 20%. The geraniol conversion at the end of the reaction (2 h for both catalysts: BW_4@MIL-101 and BW_4@aptesSiO$_2$) decreases after solid filtration, for both systems. For BW_4@MIL-101, the conversion after 2 h was only 64% (instead of 89%). After 3 h of reaction, when the oxidation of geraniol was complete in the presence of BW_4@MIL-101, only 80% of conversion was achieved when the solid was removed. Similarly, for BW_4@aptesSiO$_2$ system, the conversion was 56% after 2 h instead of 67% in the presence of heterogeneous catalyst. These results may suggest that a partial leaching of the active centres (BW_4) occurs from both supports and are lost for the solution. Both methodologies of immobilization are based on electrostatic interaction or physical absorption. This leaching phenomena was confirmed by elemental analysis, since the percentages found, after three cycles, in the case of BW_4@MIL-101 were W, 6.46; B, 0.09, and in the case of BW_4@aptesSiO$_2$ were W, 1.31; B, 0.02; Si, 29.1, which correspond to a leaching of the BW_4 peroxocomplex of 47% and 69%, respectively.

4. Conclusion

A new boron peroxotungstate $(BTBA)_4H[BW_4O_{24}]$ was prepared and characterized (FT-IR, FT-Raman, ^{11}B MAS NMR, diffuse reflectance, MALDI-MS, elemental analysis). This boron peroxotungstate (BW_4) was tested in the homogeneous oxidation of *cis*-cyclooctene, geraniol, linalool and (−)-carveol with H_2O_2 as oxidant and acetonitrile as solvent. High catalytic activity was registered for all the substrates studied under homogeneous conditions. Complete conversion of geraniol and carveol was achieved after 2 h of reaction at room temperature and 80 °C, respectively, whereas conversion of linalool reached 93% after 5 h. The selectivity for the products obtained is related with the position of the hydroxyl group in the substrate. For both geraniol and carveol, the epoxidation at the double bond nearer to the hydroxyl group is preferred. This is attributed to the possible formation of an intermediate involving the OH group, which is not favourable for linalool.

The same substrates were oxidized in the presence of the Venturello complex, $\{(PO_4)[W(O)(O_2)_2]_4\}^{3-}$ (PW_4), in the same conditions used for BW_4. The results obtained with these two peroxotungatates were not very different. Similar conversion values were obtained with both catalysts, but selectivities for the different products varied to some extent. The novel boron peroxotungstate (BW_4) was immobilized using two different strategies: (a) anchored into functionalized silica (aptesSiO$_2$) giving BW_4@aptesSiO$_2$ and (b) encapsulated on a metal organic framework, commonly referred as MIL-101, giving BW_4@MIL-101. The catalytic activity of both heterogeneous materials was investigated for geraniol oxidation and the results were compared with those obtained with BW_4 under similar, but homogeneous conditions. The encapsulated boron peroxotungstate (BW_4@MIL-101) gives rise to the best results, reaching complete conversion of geraniol after 3 h of reaction, along with 78% selectivity for 2,3-epoxygeraniol. Furthermore, BW_4@MIL-101 could be reused without appreciable loss of catalytic activity, affording similar 2,3-epoxygeraniol selectivity. BW_4@aptesSiO$_2$ and BW_4@MIL-101 were characterized after three catalytic cycles and its stability was also investigated by different characterization techniques, such as FT-IR and FT-Raman, which indicate absence of major catalyst decomposition.

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