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Dysprosium-doped zinc tungstate nanospheres as highly efficient heterogeneous catalysts in green oxidation of terpenic alcohols with hydrogen peroxide<sup>†</sup>

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A green route to oxidize terpenic alcohols (nerol and geraniol) with  $H_2O_2$  over a solid catalyst was developed. The Dy-doped ZnWO<sub>4</sub> catalyst was synthesized by coprecipitation and microwave-assisted hydrothermal heating, containing different dysprosium loads. All the catalysts were characterized through infrared spectroscopy, powder X-ray diffraction, surface area and porosimetry, transmission electronic microscopy image, and *n*-butylamine potentiometric titration analyses. The influence of main reaction parameters such as temperature, the stoichiometry of reactants, loads, and catalyst nature was assessed. ZnWO<sub>4</sub> 2.0 mol% Dy was the most active catalyst achieving the highest conversion (98%) and epoxide selectivity (78%) in nerol oxidation. The reaction scope was extended to other terpenic alcohols (*i.e.*, geraniol, borneol, and  $\alpha$ -terpineol). The highest activity of ZnWO<sub>4</sub> 2.0 mol% Dy was assigned to the lower crystallite size, higher surface area and pore volume, higher acidity strength and the greatest dysprosium load.

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## Introduction

Terpenic alcohols are abundant and renewable feedstock that has risen great interest for application in fine chemistry.<sup>1–3</sup> In particular, their oxidation and epoxidation reactions led to attractive products for perfume, fragrance, and pharmaceutical industries.<sup>4–7</sup> The presence of two oxidizable sites (*i.e.*, the hydroxyl group and the double bond) make these substrates sources of carbonylic products, and chiral compounds, which are both potential drug intermediates, thereby being valuable compounds to the fine chemical industry.<sup>8–10</sup>

Besides the use of a renewable raw material, the application of an environmentally benign oxidant makes the oxidative

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processes even more desirable and tuned with the principles of green chemistry.<sup>11</sup> In this sense, hydrogen peroxide has great advantages such as the generation of water as the only by-product, low cost, non-flammability, and easy handling. Its efficiency as an oxidant is even more prominent due to its ability to bond to the surface of a solid catalyst giving reactive oxygen species that will directly participate in oxidation reactions.<sup>12,13</sup>

Among the various catalysts used in oxidations of terpenic alcohols with hydrogen peroxide, Keggin polyoxometalates should be highlighted due to their high structural versatility that allows their use as homogeneous and heterogeneous catalysts.<sup>14–16</sup> Various metal-exchanged lacunar heteropolyacid salts (*i.e.*, cesium, potassium, or sodium) have been demonstrated to be highly efficient in the oxidation of terpenic alcohols such as geraniol, nerol, borneol, and linalool.<sup>17–19</sup>

In this sense, solid catalysts play an essential role in making the oxidation processes greener by generating fewer effluents and residues than homogeneous counterparts, reducing their environmental impact. In addition, solid catalysts can be easily recovered and reused. The doping of solid catalysts with different elements can trigger a synergism that significantly improves their efficiency in oxidation processes. For instance, zinc tungstate (ZnWO<sub>4</sub>) has been used in photocatalysis, due to

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its electronic properties, good stability, and low cost.<sup>20–22</sup> Nonetheless, their doping with rare earth elements can bring not only structural benefits, in terms of particle size and surface area, but also electronic properties, consequently increasing their catalytic activity.<sup>23</sup> Some of these properties can be interesting in oxidation reactions, such as the presence of Lewis acid sites, and high stability.<sup>24–26</sup> The use of dysprosium as a dopant has been demonstrated to be an efficient option in various oxidative processes.<sup>27</sup>

In this work, we describe the synthesis of efficient zinc tungstate catalysts doped with dysprosium by a simple coprecipitation methodology, followed by microwave-assisted hydrothermal synthesis. The catalysts were properly characterized by different methodologies and evaluated in oxidation reactions with hydrogen peroxide of various terpenic alcohols, which are renewable origin feedstock of interest for the synthesis of fragrances, fine chemicals, and drug intermediates. Nerol was the model molecule. The influence of the main reaction parameters and the reuse of the solid catalyst were assessed.

### Experimental

#### Synthesis

The catalysts were synthesized through the coprecipitation method at room temperature followed by the microwave hydrothermal method (MWH - in a microwave system of 2.45 GHz, with a maximum power of 800 W). Four catalysts with different Dy loads:  $ZnWO_4$  – pure;  $ZnWO_4$  – 0.5% Dy;  $ZnWO_4$  – 1.0% Dy and  $ZnWO_4 - 2.0\%$  Dy, were synthesized. Sodium tungstate(vi) dihydrate (Na2WO4·2H2O; 99% purity, Sigma-Aldrich), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.5% purity, Aldrich), and dysprosium(m) nitrate hexahydrate (Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O; 99.999% purity, Aldrich) were used as synthesis precursors. Firstly, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (ca. 5  $\times$  10<sup>-3</sup> mol) was dissolved in deionized water (50 mL) with constant stirring. Separately,  $Zn(NO_3)_2 \cdot 6H_2O$  (ca. 5 × 10<sup>-3</sup> mol) was dissolved in deionized water (50 mL) at pH = 6. Afterward, the  $Dy(NO_3)_3 \cdot 6H_2O$  dopant (ca. 0.5, 1.0, 2.0 mol%) was added to the aqueous solutions containing Zn<sup>2+</sup> ions, and subsequently, this solution was added to the  $WO_4^{2-}$  solution, heated at 363 K, and stirred for 30 min. Immediately, a white suspension was formed and placed in a Teflon autoclave. Finally, the Teflon autoclave containing the solution was heated in a microwave system at 413 K for 1 h. The heating rate in this system was fixed at 25 K min<sup>-1</sup>, and the pressure inside the autoclave was stabilized at 245 kPa. The formed suspension was washed with deionized water to neutralize the solution. White precipitates were collected and dried at 333 K.

#### Characterization

To assist the interpretation of the results of the catalytic tests and to verify the effects of structural properties, the catalysts were analyzed by several techniques of physical-chemical characterization.

Brunauer–Emmett–Teller (BET) and Density Functional Theory (DFT) methods were used to determine the surface area,

distribution of average diameter, and pore volume of the catalysts, respectively. The porosimetry analyses were performed on the NOVA 1200 Quantachrome equipment, using the isotherms of physical adsorption/desorption of N<sub>2</sub>, at 77 K. All catalytic materials were characterized by X-ray diffraction (XRD) using a D/Max-2500PC diffractometer (Rigaku, Japan), (Cu-K $\alpha$  radiation  $\lambda = 1.5406$  Å) in the 2 $\theta$  range from 10° to 70° at a scanning rate of 0.02° min<sup>-1</sup>. Crystallite sizes were calculated using the Scherrer equation:

$$L = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \tag{1}$$

where  $\lambda$  is the X-ray wavelength (nm),  $\beta$  is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians, and *K* is a constant related to the crystallite shape, normally taken as 0.89.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a PerkinElmer Spectrometer, model Frontier. The shape, size, and form of the nanocrystals were analyzed by high-resolution transmission electron microscopy (HR-TEM) with a Tecnai G2-F20 microscope (200 kV). The strength of the acidic sites of Dy-doped tungstate catalysts was determined by ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) performed on a CHEMBET-3000 TPR/TPD chemisorption analyzer (Quantachrome instrument). As such, 0.2 g was inserted in a U-shaped quartz tube and degassed for 1 hour under a He gas flux of 80 mL min<sup>-1</sup> (99.99%) at 393 K. After pre-treatment, the sample was cooled to 303 K, and it was kept in contact with the NH<sub>3</sub> gas flux of 40 mL min<sup>-1</sup> (99.9%) for 10 minutes, to saturate the acidic sites through the chemical adsorption of the probe molecule. Then, a He flux of 40 L min<sup>-1</sup> was set up for 10 minutes without heating, to remove an eventual physisorbed ammonia quantity, and immediately after, the material was heated up at a rate of 283 K min<sup>-1</sup> to 1173 K. Additionally, the strength of the acidic sites of Dy-doped tungstate catalysts also was determined by potentiometric titration with *n*-butylamine solution, using a BEL potentiometer (model W3B) with a glass electrode. To do this, each catalyst was suspended in acetonitrile and magnetically stirred for 3 h. In the next step, the suspension was titrated with *n*-butylamine (0.025 mol  $L^{-1}$ ) solution in acetonitrile.

#### Catalytic tests

The catalytic runs were carried out in the liquid phase with magnetic stirring, in a glass reactor coupled to the reflux condenser, heated in a water batch at atmospheric pressure. Typically,  $H_2O_{2(aq)}$  (*ca.* 34 wt%) and nerol (*ca.* 1.375 mmol) were dissolved in CH<sub>3</sub>CN (*ca.* 10 mL) and heated to 333 K. After adding the solid catalyst, the reaction was started. The reaction progress was followed for 8 h, periodically collecting aliquots that were analyzed in a Shimadzu GC-2010 Plus equipped with an AOC-20i auto-injector and a flame ionization detector (FID). All the products were duly identified and it was confirmed that spectrometry mass analysis was performed in Shimadzu GCMS-QP2010 Ultra equipment.

## **Results and discussion**

#### Characterization of the catalysts

The main structural properties of the catalysts were determined aiming to support the results of the catalytic activity of the synthesized samples. Table 1 shows the results of porosimetry analysis obtained from the adsorption/desorption of  $N_2$ .

The doping level of Dy on the zinc tungstate salts increased the surface area of these materials. The higher the Dy load, the greater the observed increase (Table 1). This effect was more noticeable when 2.0 mol% of Dy was loaded into zinc tungstate. Conversely, an increase in the Dy load led to lowering of both the volume and pore size. These two opposite effects may be closely related to the pore shape of each solid.

A plausible explanation for this increase in the surface area is that the  $Dy^{3+}$  ions may be punctually replacing  $Zn^{2+}$  ions in the crystalline structure of zinc tungstate, altering their properties. It is ascribed to the greater ionic radium of  $Dy^{3+}$  when compared to  $Zn^{2+}$  (*ca.* 102 pm and 74 pm, respectively).<sup>21</sup> The effect will be confirmed by the DRX and FT-IR analysis (Fig. 2).

The isotherms presented in Fig. 1a help to understand this phenomenon. All isotherms have a type V profile with H2 type hysteresis, which best matches weak interactions between adsorbents and adsorbates typical of micro and mesoporous materials.

Through the data in Table 1 and the pore distribution in Fig. 1b, it is possible to conclude that all the catalysts predominantly have mesopores. The key to the reported differences in surface areas may be related to the slope of the desorption curves. The  $ZnWO_4$  – pure,  $ZnWO_4$  – 0.5 mol% Dy and  $ZnWO_4$  – 1.0 mol% Dy catalysts have the same and steeper desorption branch compared to the  $ZnWO_4$  – 2.0 mol% Dy desorption branch. It may be related to a more homogeneous distribution of the accessible pores, as illustrated in Fig. 1b. This characteristic can be directly linked to the Dy load present in the catalyst.<sup>27,28</sup>

We have found that the greater the amount of Dy, the higher the heterogeneity in the distribution of pores, that is, the number of pores within a narrow range of diameters is also higher. The decrease in Dy load results in a more homogeneous distribution of the number of pores of different pore diameter ranges. However, these structural changes do not change the fact that the material is mesoporous, since most of the quantified pores belong to the region of 20 to 500 Å in diameter, characteristic of mesopores.

As can be seen in the next sections, the differences evidenced by the results of nitrogen adsorption/desorption

 Table 1
 Characterization of the catalysts through the physical adsorption of nitrogen

Catalysts	$S_{\rm BET} \left( {{{m}}^2 { m{ g}}^{ - 1}}  ight)$	$V_{\rm DFT}$ (cm <sup>3</sup> g <sup>-1</sup> )	$D_{ m DFT}$ (Å)
ZnWO <sub>4</sub> ZnWO <sub>4</sub> 0.5 mol% Dy ZnWO <sub>4</sub> 1.0 mol% Dy	59.8 59.1 60.6	0.212 0.161 0.171	122.3 93.3 93.3
ZnWO <sub>4</sub> 2.0 mol% Dy	85.2	0.187	78.0

 $S_{\rm BET}$  = surface area;  $V_{\rm DFT}$  = cumulative pore volume;  $D_{\rm DFT}$  = pore diameter.



Fig. 1 (a) Isotherms of adsorption/desorption of  $N_2$ , (b) pore diameter distribution (b) and (c) potentiometric titration curves with *n*-butylamine of the synthesized catalysts.

isotherms can be important to justify the different results achieved in nerol oxidation reactions by these catalysts.

Fig. 1c shows the potentiometric titration curves of the four synthesized catalysts. According to Pizzio and Blanco (2007),<sup>29</sup> all the catalytic materials whose solutions have an initial electrode potential between 0 and 100 mV are characterized as catalysts with strong acidic sites. Fig. 1c shows that when zinc tungstate catalysts were doped with Dy, the strength of acid sites increased. Moreover, a higher Dy load gives stronger acidity strength to the solid zinc tungstate. These results agree with the literature.<sup>30–32</sup>

Fig. 2a shows the XRD diffraction patterns of the synthesized catalysts, together with the main Miller indices, which were properly indexed to the monoclinic wolframite zinc tungstate structure according to the ICDD Card number 00-015-0774. Through this analysis, it is possible to notice the differences between the XRD diffraction profiles of different Dy-doped ZnWO<sub>4</sub> catalysts. As the amount of Dy increases in the catalyst structure, a loss of crystallinity is noticed. This factor was confirmed by calculating the crystallite size using the Scherrer equation.

The values of crystallite sizes obtained for the catalytic materials were the following: pure (24 nm), 0.5 mol% Dy (13 nm), 1.0 mol% Dy (9 nm), and 2.0 mol% Dy (7 nm). Therefore, an increase in the doping of Dy led to lower size of the crystallite.

Although an enlargement of typical diffraction peaks of  $ZnWO_4$  and a diminishment in their intensities have occurred most of them remained in the diffractograms even when the highest load of  $Dy^{3+}$  (*ca.* 2.0 mol%) was present. This behavior may be related to the size of the ionic radius of  $Dy^{3+}$ , which is larger than the radius of  $Zn^{2+}$  ions, triggering an expansion of the crystalline network of the material, mainly while a greater amount of dysprosium is doped on the  $ZnWO_4$  sites.<sup>32</sup> This different crystallinity may help to explain the different catalytic activity of these materials.



Fig. 2 Powder XRD patterns (a) and FT-IR spectra of the catalysts (b)

Fig. 2b displays the infrared spectra of the synthesized catalysts. Absorption bands placed in the region between 400 and 1050 cm<sup>-1</sup> can be visualized. At 870 cm<sup>-1</sup> close wavenumbers, a band attributed to the Zn-O-W bond vibration is noted, which is a consequence of bending and stretching deformations. The stretching vibrations of the W-O bond give absorption bands in the regions between 811 and 694 cm<sup>-1</sup>. It is possible to observe that, as the concentration of Dy increases, there is a displacement of the band close to 811 cm<sup>-1</sup> toward a higher wavenumber. This may be related to an increase in vibration energy due to the presence of Dy<sup>3+</sup> ions, which consequently led to a deformation in the material's structure, reinforcing that previously said for the XRD results.<sup>21,33</sup> Still on the FTIR spectra, the bands referring to the bending vibrations of the W-O bonds are noticed at 463 and 664 cm<sup>-1</sup> wavenumbers. Finally, the absorption bands present at 516 and 425 cm<sup>-1</sup> wavenumbers can be assigned to the symmetric and asymmetric stretching modes of the W-O and Zn-O bonds, respectively, for the ZnO<sub>6</sub> and WO<sub>6</sub> octahedral units.<sup>21</sup>

Fig. 3a–d shows the high-resolution transmission electron microscopy images of the catalytic materials. From them, it is possible to verify the contrasting differences in the shapes and particle sizes for the different solids. The profile of the pure catalyst (Fig. 3a) shows basically the nanorod structure with sizes varying between 11 and 59 nm. In contrast, as the concentration of Dy increases in each material (Fig. 3b–d), noticeable changes occur, such as an increase in the presence of nanospheres, besides the increase in particle uniformity, together with a decrease in size (0.5 mol% Dy: 2–37 nm; 1.0 mol% Dy: 3–19 nm and 2.0 mol% Dy: 3–7 nm).

It should be highlighted that when the catalysts are doped with 1.0 and 2.0 mol% Dy, they basically have nanospheres, indicating the influence of the presence of rare earth elements in the shape of the catalysts. It is important to emphasize that it



Fig. 3 TEM image of the nanocrystals: (a)  $ZnWO_4$  – pure; (b)  $ZnWO_4$  – 0.5 mol% Dy; (c)  $ZnWO_4$  – 1.0 mol% Dy and (d)  $ZnWO_4$  – 2.0 mol% Dy.

was possible to obtain nanostructured materials by simple methodologies of synthesis and with high potential in oxidation reactions.

Fig. 4 shows high-resolution TEM images (HRTEM) obtained for the tungstate catalysts. It was demonstrated that the pure ZnWO<sub>4</sub>, and ZnWO<sub>4</sub> doped with 0.5%, and 2% of Dy grew along the (002) direction with an interplanar distance of 0.250 nm, 0.256 nm, and 0.260 nm, respectively. For 1% Dy doped ZnWO<sub>4</sub> an interplanar distance of 0.363 nm was measured relative to the crystallographic plane (110). These results are consistent with the XRD technique.

Fig. 5 displays the TPD-NH<sub>3</sub> curves. Normally, it has been shown that the desorbed ammonia in the temperature ranges of 423–573 K, 573–773 K, and above 773 K was previously adsorbed on the weak, medium, and strong acid sites,



Fig. 4 HRTEM image of: (a)  $ZnWO_4 - pure$ ; (b)  $ZnWO_4 - 0.5 \text{ mol}\%$  Dy; (c)  $ZnWO_4 - 1.0 \text{ mol}\%$  Dy and (d)  $ZnWO_4 - 2.0 \text{ mol}\%$  Dy.



Fig. 5 NH<sub>3</sub>-TPD curves of ZnWO<sub>4</sub>, ZnWO<sub>4</sub> 0.5% Dy, ZnWO<sub>4</sub> 1.0% Dy and ZnWO<sub>4</sub> 2.0% Dy.

respectively.<sup>33–35</sup> The TCD signals for ZnWO<sub>4</sub>, ZnWO<sub>4</sub> 0.5% Dy, ZnWO<sub>4</sub> 1.0% Dy, and ZnWO<sub>4</sub> 2.0% Dy were integrated to assess the characteristic acidity strength of each catalyst, and the data are summarized in Table 2.

The integrated area values indicated that an increase in the Dy load increased the acidity strength. The ZnWO<sub>4</sub> 2.0% Dy catalyst displayed the highest content of medium acidity strength sites (highest area value, see Table 2). Nevertheless, the percentages of each type of acidity strength were different for each material. The ZnWO<sub>4</sub> catalyst had the highest content of medium acidic sites (84%), while the ZnWO<sub>4</sub> 0.5% Dy had the highest percentage of acidic sites of strong nature (35%).

Overall, the increase in Dy content suggests an increase in the proportion of weak acidic sites, with percentage values of 0, 8, 10, and 11% for the ZnWO<sub>4</sub>, ZnWO<sub>4</sub> 0.5% Dy, ZnWO<sub>4</sub> 1.0% Dy and ZnWO<sub>4</sub> 2.0% Dy catalysts, respectively.

#### Catalytic tests

Initially, screening to select the most active catalyst was performed. Fig. 6 shows the kinetic curves with zinc tungstate catalysts doped with different loads of dysprosium, besides the pure zinc tungstate.

Clearly, an increase in Dy load had a beneficial effect on the catalytic activity. Nonetheless, the catalyst 0.5 mol% Dy/ZnWO<sub>4</sub> had the worst performance compared to pure ZnWO<sub>4</sub>. It can be assigned to the differences of porosity between the zinc tungstate and the DY doped catalysts (Table 1), to the crystallinity and Dy load.

The pure catalyst (ZnWO<sub>4</sub>) presented the highest values of diameter and pore volume. On the other hand, an increase in Dy load had opposite effects in the porosity of doped catalysts; while the volume of pores was gradually increased with a higher load, the diameter of the pores was being decreased, mainly for

Table 2 Total integrated area of the TCD signal of the NH<sub>3</sub>-TPD profile and percentage of weak, medium, and strong acidity sites (i.e., calculated by integration of the area peaks at each specific temperature range) of the ZnWO<sub>4</sub>, ZnWO<sub>4</sub> 0.5% Dy, ZnWO<sub>4</sub> 1.0% Dy and ZnWO<sub>4</sub> 2.0% Dy catalysts

Catalysts	Total area/a.u.	Weak/%	Medium/%	Strong/%
ZnWO <sub>4</sub>	2042	0	84	16
$ZnWO_4 0.5\%$ Dy	2206	8	57	35
ZnWO <sub>4</sub> 1.0% Dy	2548	10	75	15
ZnWO <sub>4</sub> 2.0% Dy	5430	11	73	16



Fig. 6 Conversion and selectivity of nerol oxidation reactions with H<sub>2</sub>O<sub>2</sub> in the presence of zinc tungstate catalysts. Reaction conditions: nerol (1.375 mmol), H<sub>2</sub>O<sub>2</sub> (2.750 mmol), temperature (333 K), catalyst (15 mg), CH3CN (10 mL)

the highest load of Dy (Table 1). Therefore, when we correlate only the activity of Dy doped ZnWO4 catalysts, we concluded that the catalyst with the largest volume of pores (ca. 0.187 cm<sup>3</sup> g<sup>-1</sup>) was the most active. When we verified the volume of the pores of the undoped catalyst we realize that its pores are still bigger (ca. 0.210 cm<sup>3</sup> g<sup>-1</sup>) than the most active catalyst. It may explain the high activity of pure ZnWO<sub>4</sub>. Another key aspect is that the tungstate catalyst can itself catalyze oxidations with hydrogen peroxide.<sup>20</sup> Conversely, the catalyst with the lowest Dy load was less active due to its pores with the lowest volume.

However, the Dy load plays an essential role too. When the catalysts are doped with a load higher than 0.5 mol% Dy, this additional active site is present in enough amounts to compensate for the reduction of the pore volume of ZnWO<sub>4</sub> triggered by the Dy load. The crystallinity of doped catalysts provides too important insights. An increase in Dy load diminished the size of the crystallite. Applying the Scherrer equation to the most intense diffraction peaks (Fig. 2a) the following values were obtained: 0.5 mol% Dy (13 nm), 1.0 mol% Dy (9 nm), and 2.0 mol% Dy (7 nm). This effect was attributed to the greater size of the ionic radius of Dy<sup>3+</sup> ions when compared to the Zn<sup>2+</sup> cations. The doping of Dy triggers an expansion of the crystalline network of the material, mainly when at higher loads.<sup>32</sup> This lower crystallite size may improve the ability of materials for binding with H2O2 molecules, which can increase the formation of reactive oxygen species.<sup>30,31</sup>

#### Paper

Another important factor that may be influencing nerol oxidation is the acidity of the catalysts. According to the results presented by  $NH_3$ -TPD (Fig. 4), the total acidity is proportional to the amount of Dy, thus, the ZnWO<sub>4</sub> catalyst 2.0% Dy, which presented the greatest number of acidic sites (Table 2), was the most active. It is interesting to note that the distinct types of acidic sites (*i.e.*, weak, medium, and strong) can have different effects on the activity of Dy catalysts in the oxidation reactions. Among the used catalysts, those with the highest percentage in medium acidity strength sites were those that showed the best performance in the nerol oxidation. The presence of acidic sites on the catalyst surface can be essential for the interaction of the peroxide oxidant with the substrate.<sup>30</sup>

Scheme 1 describes a probable reaction pathway involving the peroxidation of the Dy doped-zinc tungstate catalyst (*i.e.*,  $Dy_{3/2}(Zn)WO_4$ ) and the allylic oxidation assisted by the hydroxyl group.<sup>30,31,38</sup>

In allylic alcohol oxidation reactions, the active species commonly formed are the metal-peroxide intermediates. The metal acts as a Lewis acid, binding to an oxygen atom of  $H_2O_2$ . While an oxygen atom of the oxidant linked to the metal peroxide the olefin double bond, the oxygen atom of the allylic hydroxyl group is bonded to the metal. Thus, the O-O bond cleavage of the peroxide group occurs and, consequently, the epoxide is formed with the release of the catalyst.<sup>31,38</sup>

Fig. 6 shows the conversion and selectivity of the reaction products. Nerol has two potentially oxidizable sites; the carbonyl group which can be oxidized to aldehyde, and a double bond, which may be epoxidized. We have found that regardless of catalyst, nerol epoxide was always the major product, neraldehyde being the minor product. Oligomers, which are not detectable by the GC analysis, were formed in all the reactions, as evidenced by the mass balance of reaction. Once the most active catalyst is selected, we have investigated the effect of the amount of catalyst on the conversion and selectivity of products. Kinetic curves and selectivity of reactions are presented in Fig. 7.

An increase in the amount of  $ZnWO_4 2.0 \text{ mol}\%$  Dy catalyst enhanced the initial rate and the final conversion of the reactions. This effect can be attributed to the higher number of active sites present in the reaction when a higher mass of catalyst is used. On the other hand, with a load higher than 15.0 mg, the selectivity for oligomers shows a drastic increase. It is a consequence of the noticeable decomposition underwent by



Scheme 1 Hydroxyl group-assisted allylic oxidation of nerol with hydrogen peroxide in the presence of  $Dy^{3+}$  doped zinc tungstate catalyst (adapted from ref. 38).



Fig. 7 Conversion and selectivity of nerol oxidation reactions with  $H_2O_2$  in the presence of different amounts of  $ZnWO_4 - 2.0\%$  Dy catalyst. Reaction conditions: nerol (1.375 mmol),  $H_2O_2$  (2.750 mmol), temperature (333 K), CH<sub>3</sub>CN (10 mL)

the oxidant, diminishing the efficiency of oxidation, a fact that occurred mainly when 30 mg of catalyst was used.

The catalytic performance of  $ZnWO_4 - 2.0 \text{ mol}\%$  Dy in nerol oxidation reactions with hydrogen peroxide was compared with various metal oxide and heteropolyacid catalysts (see Fig. SM1, ESI†). It was found that the Dy/ZnWO<sub>4</sub> catalyst was more active and selective than other metal oxide catalysts (see ref. ESI†).<sup>36,37</sup> Only the heteropolyacid salt (*i.e.*, Na<sub>7</sub>PW<sub>11</sub>O<sub>39</sub>) was more efficient, however, it was totally soluble in the reaction medium.<sup>19</sup>

The impact of the molar ratio of the oxidant to the substrate was also assessed (Fig. 8). Since the reaction was highly efficient with a low load of the oxidant, this effect was assessed only at three levels. At an equimolar stoichiometric amount (*ca.* 1:1), the oxidation was slightly compromised; a lower selectivity toward the main product (*i.e.* nerol epoxide) was achieved. Even an isomerization product (*i.e.*, geraniol) was formed under these conditions, although with a low selectivity (*ca.* 4%). Besides, the highest neraldehyde selectivity was reached with this load of the oxidant. When a 1:1.5 or 1:2 molar ratio of nerol to the oxidant was used, no significant



Fig. 8 Conversion and selectivity of nerol oxidation reactions with different amounts of  $H_2O_2$  in the presence of  $ZnWO_4$  2.0 mol% Dy catalyst. Reaction conditions: nerol (1.375 mmol), catalyst (15 mg), temperature (333 K), CH<sub>3</sub>CN (10 mL).

difference was observed in both conversion and reaction selectivity.

The influence of temperature was assessed, without overtaking the boiling point of acetonitrile (Fig. 7). The initial rate of reaction was very sensitive to the increasing temperature, as was also observed for the conversion of the reactions.

Conversely, varying the reaction temperature we noticed that the selectivity of products remained almost untouchable (Fig. 9). Neraldehyde and mainly the nerol epoxide were two oxidation products formed (Scheme 2).

The reaction scope was extended to the other terpenic alcohols and the main results are shown in Fig. 8. The results of the nerol oxidation were compared to those obtained with different alcohols; geraniol (*i.e.*, allylic primary alcohol and geometric isomer of the nerol), borneol (*i.e.*, secondary bicyclic alcohol), and  $\alpha$ -terpineol (unsaturated tertiary alcohol) (Fig. 10).

The substrates were chosen because they have hydroxyl groups and double bonds with different reactivity. The pair (*Z*) nerol and (*E*) geraniol are the *cis* and *trans* isomers, respectively. Although both have been completely consumed (*ca.* 100%, after 8 h), and both had been converted to aldehydes with the same selectivity, their double bonds presented different reactivity, revealing that the reaction selectivity was distinct. While the geraniol provided two epoxide products (*i.e.*, geraniol epoxide and geraniol diepoxide) (Scheme 3), the nerol provided only the epoxide product (Scheme 2).

Firstly, it is important to highlight that although Tatsumi *et al.* previously described that the oxidation reaction of these alcohols toward aldehydes is minimized, attributing it to the



Fig. 9 Conversion and selectivity of nerol oxidation reactions with  $H_2O_2$  in the presence of ZnWO<sub>4</sub> – 2.0 mol% Dy catalyst at different temperatures. Reaction conditions: nerol (1.375 mmol),  $H_2O_2$  (2.750 mmol), catalyst (15 mg), CH<sub>3</sub>CN (10 mL).



Scheme 2 Oxidation reaction of nerol to nerol epoxide and neraldehyde.



Fig. 10 Conversion and selectivity of different substrate oxidation reactions with  $H_2O_2$  in the presence of ZnWO<sub>4</sub> 2.0 mol% Dy catalyst. Reaction conditions: nerol (1.375 mmol),  $H_2O_2$  (2.750 mmol), temperature (333 K), catalyst (15 mg), CH<sub>3</sub>CN (10 mL).



Scheme 3 Oxidation reaction of geraniol to geranaldehyde, geraniol epoxide and geraniol diepoxide.

presence of the allylic hydroxyl groups.<sup>21</sup> Therefore, the preferential formation of epoxides could be expected. Recently, we have assessed the oxidation of terpenic alcohols over niobium catalysts and verified the same effect.<sup>38</sup>

On the other hand, the literature describes that epoxidation of this double bond is a hydroxyl group-assisted reaction.<sup>39</sup> In oxidation reactions of the geraniol by hydrogen peroxide over tungsten, titanium, niobium or vanadium oxide catalysts, the coordination of metal oxide catalysts to the olefin double bond, as well as the peroxidation of the metal are always involved.<sup>34,35</sup> The peroxidation step of the niobium catalyst and the interaction with the organic substrate are attributed to the different species of active sites present in the niobium catalyst. Lewis acid sites and Brønsted acid sites allow the simultaneous adsorption of the oxidant and the organic substrate even in the presence of water.<sup>40</sup> Herein, we suppose that both tungsten and dysprosium are active sites for this reaction.

The different chemoselectivity of the oxidation reactions of geraniol and nerol can be assigned to the steric hindrance effects on the double bond of nerol (*i.e.*, *cis* isomer). It hampers the epoxidation that led to diepoxide. Conversely, in the *trans* isomer (*i.e.*, geraniol), this effect is absent and the diepoxide is easily formed.<sup>41</sup>

Compared to the geraniol and nerol, the reactivity of  $\alpha$ -terpineol was significantly lower; only 35% conversion was achieved. However, even with a tertiary alcohol, two oxidation products were formed. In the presence of ZnWO<sub>4</sub> 2.0 mol% Dy catalyst, the double bond of terpineol was epoxidized providing the  $\alpha$ -terpineol epoxide (Scheme 3). Even in a lower yield than that

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achieved in the reactions of nerol and geraniol, an epoxidation product was formed. The lower epoxide formation when compared to the other two terpenic alcohols can be attributed to the absence of the hydroxyl group in the allylic position to the double bond, which assists this kind of epoxidation. In addition, a rare cyclization reaction of this epoxide led to the formation of *p*-mentan-2-ol, 1,8 epoxide (Scheme 4).

The formation of this bicyclic compound can be assigned to the nucleophilic attack of the hydroxyl group on the trisubstituted carbon of  $\alpha$ -terpineol epoxide, which provokes the rupture of the oxirane ring, followed by the prototropism between the hydroxyl group and the oxygen atom of the epoxide. Previously it was revealed that 1,2-epoxy-cyclohexanes exist in a half-chair conformation, and the hydroxy-substituted isopropyl groups then require this conformation for a nucleophilic attack on the epoxide.<sup>42</sup>

The reaction between borneol and hydrogen peroxide in the presence of the  $ZnWO_4 - 2.0\%$  Dy catalyst was highly selective toward the carbonylic product (*ca.* 100% selectivity, Fig. 8), exclusively leading to camphor formation (Scheme 5).

The lower conversion achieved in borneol oxidation (*ca.* 60%) when compared to the oxidation of other alcohols is a consequence of different reactivity of hydroxyl groups. While geraniol and nerol have primary hydroxyl groups, borneol has the secondary one. The total conversion of the borneol occurred after longer reaction times (*ca.* 20 h).

The reusability of the  $ZnWO_4$  2.0 mol% Dy catalyst was assessed. Kinetic curves and the main results of conversion and selectivity are shown in Fig. 11.

Although omitted in Fig. 11, a high recovery rate of the catalyst was achieved in all the recycles (ca. > 95%), indicating that the procedure used was very efficient. After the first cycle of reuse, there was a gradual decrease in the conversion of reactions, which was followed during three cycles of recovery/ reuse. In terms of selectivity, it was noticed that until the second cycle it remained basically constant, however, in the



**Scheme 4** Oxidation reaction of  $\alpha$ -terpineol to *p*-menthan-2-ol, 1,8-epoxy and  $\alpha$ -terpineol epoxide.



Scheme 5 Oxidation reaction of borneol to camphor.



Fig. 11 Evaluation of the efficiency in the nerol ns in recovery and recycling tests of the  $ZnWO_4$  2.0 mol% Dy catalyst with  $H_2O_2$  oxidation reaction. Reaction conditions: nerol (1.375 mmol),  $H_2O_2$  (2.750 mmol), temperature (333 K), catalyst (15 mg),  $CH_3CN$  (10 mL).

third cycle it was verified that the oxidation became less efficient, with a consequent increase in the formation of oligomers.

Aiming to investigate the reason for the loss in activity of the catalyst after the successive reuses, analyses of XRD patterns and infrared spectroscopy were performed. A comparison of reused and fresh catalyst is shown in Fig. 12 and 13.

As shown in Fig. 10, the diffractogram profile of the reused catalyst showed some differences in relation to the fresh



Fig. 12 Powder XRD patterns of a fresh and reused  $ZnWO_4$  2.0 mol% Dy catalyst in nerol oxidation reactions with  $H_2O_2$ . Reaction conditions: nerol (1.375 mmol),  $H_2O_2$  (2.750 mmol), temperature (333 K), catalyst (15 mg), CH<sub>3</sub>CN (10 mL).



Fig. 13 Infrared spectra of the fresh and reused ZnWO<sub>4</sub> 2.0 mol% Dy catalyst in nerol oxidation reactions with  $H_2O_2$ . Reaction conditions: nerol (1.375 mmol),  $H_2O_2$  (2.750 mmol), temperature (333 K), catalyst (15 mg), CH<sub>3</sub>CN (10 mL).

catalyst. With the aid of calculating the crystallite size, it is possible to evaluate the difference between the two materials. The fresh catalyst presents a crystallite size of approximately 7 nm, while after the fourth run this size was increased to 13 nm. Once we had previously demonstrated that the lower the crystallite size, the higher the catalytic activity, which partly explains the loss of activity of the ZnWO<sub>4</sub> 2.0 mol% Dy catalyst.

In previously published works, the authors found that crystallinity is a factor that can make the difference in catalytic activity. It was found that in materials with less crystallinity and smaller crystallite size, there is a higher ability to interact more easily with hydrogen peroxide molecules, which consequently leads to the cleavage of O–O bonds in a greater number of reactive oxygen species that will directly contribute to the oxidation process.<sup>18,30,34</sup>

On the other hand, comparing the bands referring to the bending of the W–O bonds (*ca.* 463 cm<sup>-1</sup>), and the symmetric and asymmetric stretching modes of the W–O and Zn–O bonds (*ca.* 516 and 425 cm<sup>-1</sup> wavenumbers), present in the infrared spectrum of the fresh catalyst, and the bands present in the spectrum of the used catalyst, it is possible to see that they were shifted. This suggests that the ZnO<sub>6</sub> and WO<sub>6</sub> octahedral units, respectively, undergone a distortion, possibly caused by the loss of Dy ions. In addition to this effect, it is possible also that the size of the nanoparticles has undergone an increase, due to heating in the recycling process and due to the coalescence effect caused in the reaction medium.

The leaching of the catalyst was also assessed as reported in the literature.<sup>43-46</sup> Due to the difficulty of detecting the Dy<sup>3+</sup> ions in solution, two sets of experiments were performed (see Fig. SM2 and SM3, ESI<sup>†</sup>). The following approaches were used to evaluate the leaching. In the first one, two solutions with only acetonitrile were heated for 30 minutes, one containing the pure zinc tungstate catalyst and the other containing the Dy<sup>3+</sup>-doped zinc tungstate catalyst. Afterward, the catalysts were removed, and the reactions proceeded for 8 h. While the first reaction was almost stopped, the second one proceeded to achieve a conversion of 80%. It is suggestive that Dy<sup>3+</sup> ions truly are being leached to the solution (Fig. 2SM and 3SM, ESI†). Additionally, a second test was performed with the two catalysts; they were heated for 30 minutes in a solution containing the oxidant and substrate, after that, the catalysts were removed (i.e., pure, or doped zinc tungstate), and the reaction was monitored for 8 h. Once, the results confirmed the Dy<sup>3+</sup> leaching, indicated by the conversion of 80%. However, different than verified with acetonitrile, there was also leaching of zinc tungstate, although lower than the leaching of the Dy-doped catalyst. It was revealed that the presence of the aqueous solution of the oxidant increased the leaching of both catalysts (i.e., pure, and doped zinc tungstate).

## Conclusions

ZnWO<sub>4</sub>–Dy catalysts were efficiently synthesized by co-precipitation followed by the microwave-assisted hydrothermal heating method,

with controlled morphological properties, which demonstrated to be effective catalysts for the selective epoxidation of allylic terpenic alcohols with hydrogen peroxide. Reactions were carried out in the presence of a dysprosium doped zinc tungstate solid catalyst (ca. 0.5; 1.0, 2.0 mol% Dy), and hydrogen peroxide, a cheap and green oxidant. ZnWO<sub>4</sub> 2.0 mol% Dy was the most active and selective catalyst, a consequence of the lowest crystallite size, and the highest surface area, pore volume, and Dy load. As described for tungsten, niobium, or titanium catalysts, the epoxidation of allylic terpenic alcohols (*i.e.*, nerol and geraniol) with  $H_2O_2$  is a hydroxy-assisted reaction. The different stereochemistry of nerol and geraniol revealed that only the geraniol was converted to epoxide and diepoxide products. The reactivity of other terpenic alcohols was also evaluated. Noticeably, the double bond of  $\alpha$ -terpineol was epoxidized, and after undergoing a nucleophilic attack of the hydroxyl group led to the formation of a rare product (i.e., p-mentan-2-ol, 1,8 epoxide). Borneol was selectively converted to camphor, however, since that it is a secondary alcohol, its total conversion occurred after longer reaction times (ca. 20 h). The reusability of the ZnWO<sub>4</sub> 2.0 mol% Dy catalyst was investigated. High recovery rates (ca. 95%) were obtained. After recovery, the solid catalyst was reused without loss of selectivity, however, there was a decrease of conversion after the third run. Infrared spectroscopy analysis and XRD patterns of the reused catalyst showed that the crystallite size of the recovered catalyst was increased, which compromised their activity.

## Conflicts of interest

There are no conflicts to declare.

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