

# The chemical reactivity of some terpenes investigated by alumina catalyzed epoxidation with hydrogen peroxide and by DFT calculations

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## Abstract

The selectivity of the alumina catalyzed epoxidation of (*S*)-limonene, citronelal, citral, citronelol and (1*S*)-(α)-pinene with aqueous 70 wt% and anhydrous 24 wt% hydrogen peroxide is described. DFT molecular orbital calculations were used aiming at a better understanding of the reactivity of these terpenes. The more nucleophilic carbon–carbon double bond, which has a higher molecular orbital energy, is preferentially epoxidized (site-selectivity). Furthermore, a preference for epoxidation in competition with other possible reactions is observed for citronelal, citral, citronelol and (1*S*)-(α)-pinene (chemo-selectivity). Nonetheless, we were not able to achieve a stereo-selective epoxidation of the terpenes using alumina and hydrogen peroxide.

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**Keywords:** Epoxidation; Terpenes; DFT calculation; Alumina; Hydrogen peroxide

## 1. Introduction

Terpenes are natural and sustainable feedstocks for the fine chemical industry, as they can be used as intermediates and ingredients for flavours, fragrances and pharmaceuticals [1]. The epoxidation of terpenes is an attractive chemical transformation as these epoxides are versatile building blocks [1]. Several reviews are available in the recent literature concerning more environmental friendly ways to do epoxidations [2–4]. However, even nowadays the most useful way to obtain epoxides is the reaction between a peracid and the desired olefin, which cannot be considered an environmental friendly process due to the formation of stoichiometric amounts of the corresponding acid [2].

The use of terpenes as starting materials for fine chemical synthesis requires selective methodologies of epoxidation since terpenes contain alkene functional groups with different degrees of substitution and, in addition, they have other functionalities which can be oxidized and/or effect the chemistry of the carbon–carbon double bonds [5,6].

Aluminas have been used by organic chemists as catalysts or as supports for reagents and catalysts to obtain fine chemicals [7,8]. We have shown that alumina itself is already active for the epoxidation of nucleophilic alkenes with anhydrous hydrogen peroxide, obtaining selectivities in the 70–90% range [9]. The epoxidation activity of alumina has already been reported [10], however, the reactions showed low epoxide yields and used a large excess of alumina and oxidant.

In this report, we describe the site-, chemo- and stereo-selectivity of the alumina catalyzed epoxidation of some terpenes ((*S*)-limonene, citronelal, citral, citronelol and (1*S*)-(α)-pinene) with hydrogen peroxide and perform density functional calculations in order to achieve a better understanding of the different selectivities observed.

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## 2. Experimental

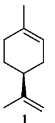
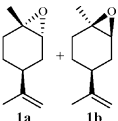
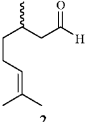
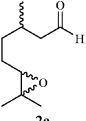
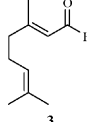
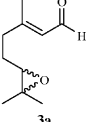
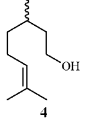
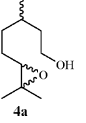
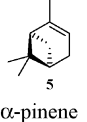
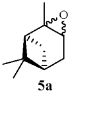
### 2.1. Materials

The terpenes (*S*)-limonene (Fluka, 97%), citronelal (racemic mixture, Merck, 94%), citral (Merck, 99%, mixture of 40% *cis* and 60% *trans* isomer), citronelol (racemic mixture, Merck, 98%) and (1*S*)-( $\alpha$ )-pinene (Aldrich, 99%) (Table 1) were used as purchased without further treatment. Hydrogen peroxide (70 wt%) was provided by Peróxidos do Brasil (Solvay). Anhydrous hydrogen peroxide (24 wt%) in ethyl acetate was prepared by azeotropic distillation [9]. Commercial alumina (Fluka, type 507C, neutral, 100–125 mesh) and a sol–gel alumina (SG) calcined at 400 °C, prepared and characterized as described elsewhere [11], were used as epoxidation catalysts.

### 2.2. Catalytic epoxidation of terpenes

A mixture containing the terpene (20.0 mmol), anhydrous 24 wt% or aqueous 70 wt% hydrogen peroxide (40 mmol), di-*n*-butyl ether (5.00 mmol, internal standard) and ethyl acetate (10 mL) was placed into a two-necked round-bottomed flask and heated under reflux with magnetic stirring for 1 h. A sample was taken for GC analysis and the reaction started by addition of alumina (100.0 mg). Aliquots of the reaction mixture were taken after the indicated reaction times for a total of 6 h. These aliquots (50  $\mu$ L) were diluted in ethyl acetate (2 mL, Merck, p.a.), treated with a few milligrams of manganese dioxide, for decomposition of the peroxides and then with anhydrous sodium sulfate, to remove residual water. These solutions were then injected into a Hewlett-Packard HP 5890 Series II gas chromatograph, equipped with a flame ionization detector and a HP Ultra

Table 1  
Alumina catalyzed epoxidation of the terpenes with anhydrous 24 wt% and aqueous 70 wt% H<sub>2</sub>O<sub>2</sub>

Entry	Al <sub>2</sub> O <sub>3</sub>	Substrate	Major products	Conversion (%) at 5 h		Selectivity (%) at 5 h <sup>a</sup>	
				Anhydrous	Aqueous	Anhydrous	Aqueous
1	Fluka	 1 ( <i>S</i> )-limonene	 1a + 1b	30	25	78 <sup>b</sup>	73 <sup>b</sup>
2	SG			40	35	80 <sup>b</sup>	70 <sup>b</sup>
3 <sup>c</sup>	Fluka	 2 Citronelal	 2a	35	27	60	30
4 <sup>c</sup>	SG			60	37	65	31
5 <sup>d</sup>	Fluka	 3 Citral	 3a	38	33	55	50
6 <sup>d</sup>	SG			41	38	62	66
7	Fluka	 4 Citronelol	 4a	23	20	57	97
8	SG			42	47	65	73
9 <sup>e</sup>	Fluka	 5 $\alpha$ -pinene	 5a	30	25	57	63
10 <sup>e</sup>	SG			32	30	62	57

<sup>a</sup> Selectivities for the major products.

<sup>b</sup> Sum of internal and external monoepoxides and diepoxides corresponds to 97–99% of products formed.

<sup>c</sup> 3,7-Dimethyloctanoic acid, 6,7-dihydroxy-3,7-dimethyloctanoic acid and 6,7-dihydroxy-3,7-dimethyloctanal were also detected in the oxidation of the citronelal.

<sup>d</sup> 3,7-Dimethyloctan-2,6-dienoic acid and 5-(3,3-dimethyloxiran-2-yl)-3-methylpenten-2-oic acid were also detected in the oxidation of the citral.

<sup>e</sup>  $\alpha$ -Campholenic aldehyde and 2,6,6-trimethylbicyclo[3.1.1]heptane-2,3-diol were also detected in the oxidation of the (1*S*)-( $\alpha$ )-pinene.

2 capillary column (25 m × 0.2 mm × 0.33 μm film thickness). Products were quantified using calibration curves previously obtained with standard solutions. The products were also analyzed by electrospray ionisation-mass spectrometry (ESI-MS) using a Q-Trap LC-MS/MS system from Applied Biosystems, operating in the positive mode.


### 2.3. Electronic structure calculation

The DFT calculations were done using a CAChe Worksystem Pro Version 6.01 program with DGauss package. The structures of hydrogen peroxide and the terpenes were refined by performing a geometry optimization calculation in DGauss using the B88-LYP GGA functional with the 6-31G\*\* basis set. All of the molecular orbitals, occupied and unoccupied, were generated by a DGauss/DFT wavefunction for the studied molecules.

## 3. Results and discussion

The distinction between thermodynamic and kinetic stability must always be in our minds when we want to understand the chemical reactivity of a group of molecules. It is very important to realize that a molecule thermodynamically more stable than another one is not necessarily less reactive. Indeed, it might be more reactive or, one might say, kinetically less stable. Reactivity is determined by a number of factors but one of them is the energy of the molecular orbital of the site where the chemical transformation is going to happen, in this case a carbon–carbon double bond. On the other hand, thermodynamic stability is determined by the energies of all filled orbitals [12]. Hence, frontier orbital analysis is a very important tool in order to try to understand chemical reactivity in terms of the kinetic stability of the functionalities in a molecule. The interactions of a molecular orbital in the transition state of a chemical reaction take the kinetic effects of a chemical transformation into account and can be a means for reaction selectivity when a molecule has several chemical functionalities.

The epoxidation of a carbon–carbon double bond may occur via two possible molecular orbital interactions between a peroxy species and an olefin, as shown in Fig. 1. In the first molecular orbital interaction (Fig. 1A) the peroxy species is an electrophile. This interaction usually takes place between an electron-rich carbon–carbon double bond and an electron deficient peroxy species (e.g., M–OH or

 [13]. The second possible interaction (Fig. 1B) occurs when an electron-deficient carbon–carbon double bond and an electron-rich peroxy species (e.g., HOO<sup>−</sup>) are involved. However, it is important to point out that both these interactions represent extremes and that both types of interaction can happen simultaneously in the transition state [14]. This synergism may help to lower the transition state energy, which means that the chemical transformations are kinetically favoured. Of course, other interactions involving other orbitals from other chemical functionalities, e.g., from the alcohol and aldehyde groups, may occur, which means that the chemo-selectivity is determined by a small difference of energy

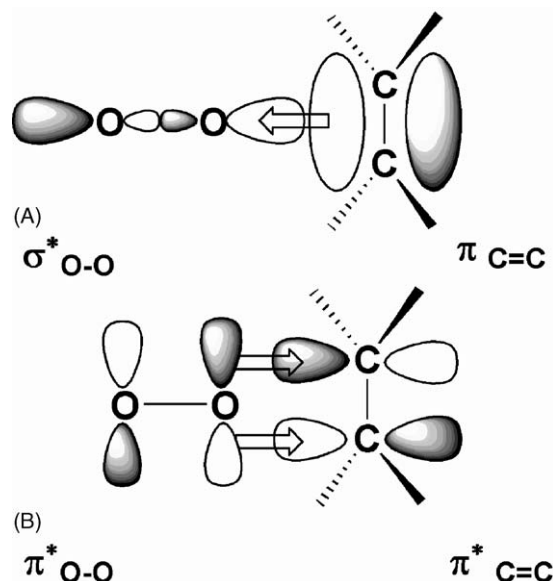


Fig. 1. Molecular orbital interactions between the carbon–carbon double bond and a peroxy species: (A) acceptor interaction involving the occupied  $\pi_{C=C}$  of an alkene and the vacant  $\sigma_{O-O}^*$  orbital of a peroxy species; (B) (back)-donation interaction involving a lone pair of the distal oxygen atom in a peroxy species and an empty  $\pi_{C=C}^*$  orbital of an alkene.

between the molecular orbitals of the peroxy species and the molecular orbitals of the desired reactive functionality.

The conversions and selectivities of the epoxidation of terpenes with anhydrous (24 wt%) and aqueous (70 wt%) hydrogen peroxide are shown in Table 1. The reactions catalyzed by SG alumina resulted in higher conversions, as also observed in our previous papers [11,17,18]. A conversion ranging from 2% to 5% was observed in the absence of a catalyst, confirming that alumina is catalytically active for the epoxidation of these substrates. A filtration experiment showed that the catalyst was heterogeneous, since no further reaction took place in the filtrate. The selectivities for epoxides using aqueous 70 wt% were lower in most of the epoxidations of terpenes, as these epoxides are prone to hydrolysis, rearrangements or further oxidation (e.g., the aldehyde moiety oxidizes to carboxylic acid) in the presence of water.

The profile of the (*S*)-limonene epoxidation is shown in Fig. 2. The major products of this reaction are the diastereoisomers **1a** and **1b**. The selectivity for these 1,2-epoxides is very high in the beginning of the reaction. However, during the reaction it drops to 80% due to the formation of the diepoxide **1d**. The approach of the 1,2-epoxides to the alumina surface is probably easier due to their higher polarity compared to (*S*)-limonene, which enables the further epoxidation of the C<sub>(7)</sub>–C<sub>(8)</sub> site. The diastereoisomeric ratio of **1a** and **1b** is 1.16, indicating a low diastereo-selectivity, caused by the steric hindrance of the isoprenyl group at the most favoured 1,2-position. The same tendency was previously observed with other catalysts [15,16].

It is interesting to see that the external carbon–carbon double bond has less steric hindrance than the internal carbon–carbon double bond (Fig. 3). However, a strong preference for the epoxidation of the carbon–carbon double bond at C<sub>(1)</sub>–C<sub>(2)</sub>

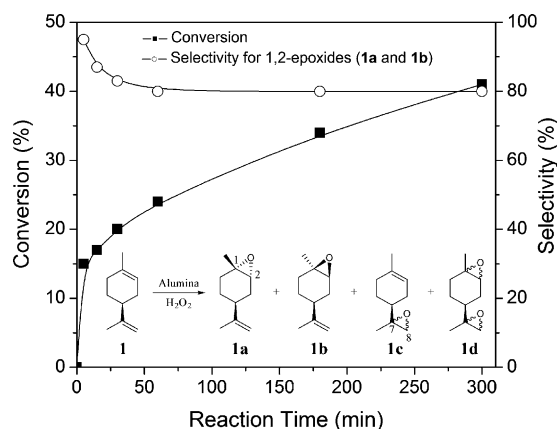


Fig. 2. Epoxidation of (*S*)-limonene. Reaction conditions: 100 mg of SG alumina calcined at 400 °C, 20 mmol of (*S*)-limonene, 40 mmol of anhydrous H<sub>2</sub>O<sub>2</sub> 24 wt%, 80 °C.

instead of C<sub>(7)</sub>–C<sub>(8)</sub> is observed. This can be predicted by DFT quantum molecular calculations. The most nucleophilic site of (*S*)-limonene is the 1,2-position, as indicated by its higher molecular orbital energy (−4.97 eV, HOMO). The external double bond is less nucleophilic as shown by its lower molecular orbital energy (−5.31 eV, HOMO-1). Although, the difference of 0.34 eV might seem to be small at first, this value corresponds to a difference of ca. 32.8 kJ mol<sup>−1</sup> between these molecular orbitals, which causes a strong kinetic effect [12]. Therefore, the higher selectivity for the 1,2-epoxides (**1a** and **1b**) is controlled by electronic instead of steric effects.

Despite lack of experimental proofs for active peroxy species on the alumina surface, the hydrogen peroxide activation certainly occurs by means of acid sites, such as

Al–OH [17]. The extension of this interaction is not totally understood, but the hydration of the surface seems to be a very important factor to understand the catalytic activity of the alumina surfaces [17,18]. For this study, we consider as a rough approximation that the terpenes react directly with hydrogen peroxide. As proposed in Fig. 1 both interactions involving HOMO(H<sub>2</sub>O<sub>2</sub>) → LUMO(olefin) and HOMO(olefin) → LUMO(H<sub>2</sub>O<sub>2</sub>) occur synergistically; however, the preferred interaction is between HOMO(olefin) and LUMO(H<sub>2</sub>O<sub>2</sub>) as its Δ*E* is lower (4.21 eV) than for the HOMO(H<sub>2</sub>O<sub>2</sub>) → LUMO(olefin) interaction (4.97 eV). It is important to point out that the interaction of H<sub>2</sub>O<sub>2</sub> with the alumina surface should make the O–O bond more electrophilic, as the acidity of the surface seems to have a very important role in alumina catalyzed epoxidation [17] (Fig. 4).

The profile of the citronelal epoxidation is shown in Fig. 5. The major product of this reaction is the epoxide **2a**. The high initial selectivity for this epoxide is surprising as one would expect that the aldehyde group would also oxidize to the carboxylic acid.

The initial high selectivity for the epoxide can be also understood through the energy of the molecular orbitals related to the alkene and aldehyde functionalities (Fig. 6). The alkene (−5.13 eV) is slightly more nucleophilic than to the aldehyde group (−5.21 eV), explaining the preference for epoxidation rather than aldehyde oxidation at initial reaction times. It should also be considered that in the beginning of the reaction the aldehyde group may moderately interact with the alumina surface, thus making this group less nucleophilic and disfavoring its oxidation (vide infra Fig. 9). However, as water is not removed during the reaction, this interaction with the surface becomes weaker due to the competition with water for the alu-

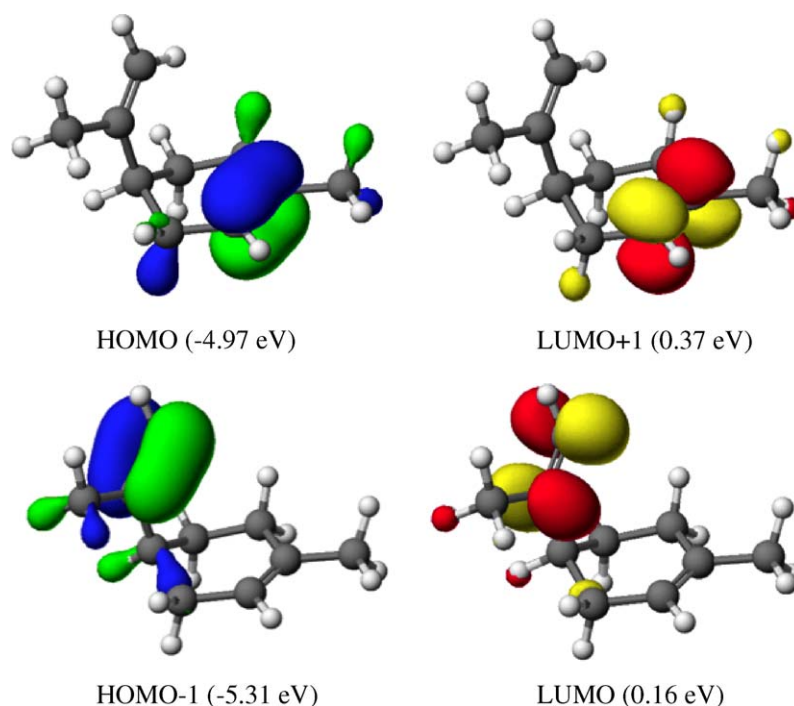


Fig. 3. Frontier molecular orbitals of the (*S*)-limonene.

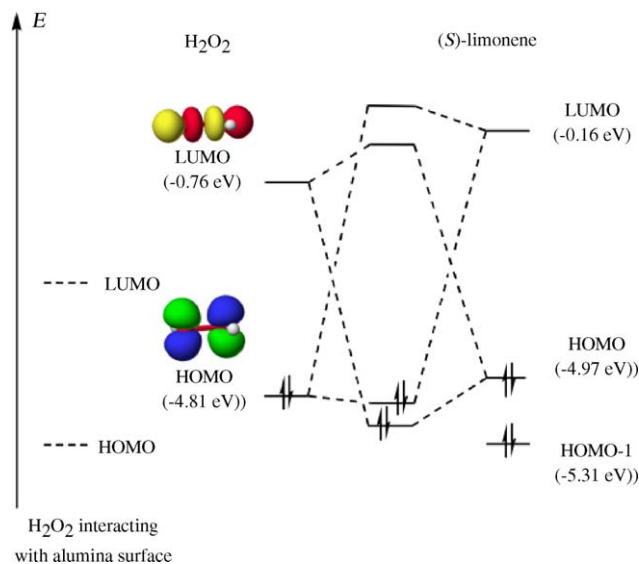


Fig. 4. Frontier molecular orbital interaction between  $\text{H}_2\text{O}_2$  and (S)-limonene.

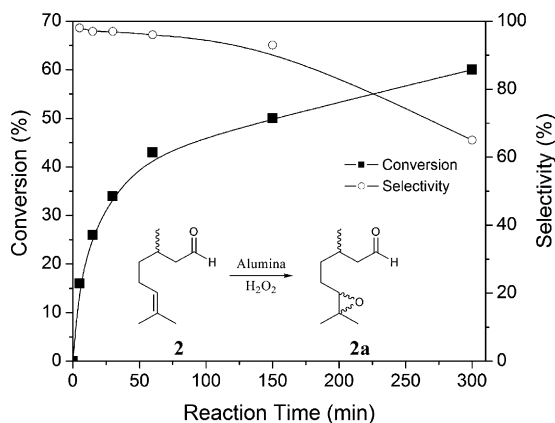


Fig. 5. Epoxidation of citronelal. Reaction conditions: 100 mg of SG alumina calcined at  $400^\circ\text{C}$ , 20 mmol of citronelal, 40 mmol of anhydrous  $\text{H}_2\text{O}_2$  24 wt%,  $80^\circ\text{C}$ .

mina surface sites. Also, with the rehydration of the alumina surface the approach of the alkene to the active sites becomes a limiting step [17,18], which means that at longer reaction times the epoxidation becomes disfavoured and the oxidation of the aldehyde is favoured. By ESI-MS we observed the forma-

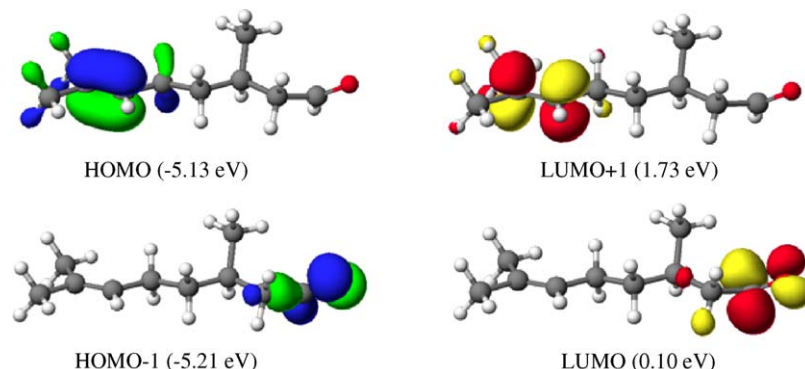


Fig. 6. Frontier molecular orbitals of citronelal.

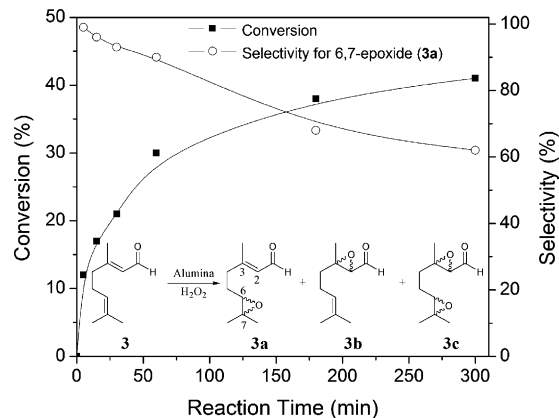


Fig. 7. Epoxidation of citral. Reaction conditions: 100 mg of SG alumina calcined at  $400^\circ\text{C}$ , 20 mmol of citral, 40 mmol of anhydrous  $\text{H}_2\text{O}_2$  24 wt%,  $80^\circ\text{C}$ .

tion of 3,7-dimethyloct-6-enoic acid ( $m/z = 170$ ), 6,7-dihydroxy-3,7-dimethyloctanoic acid ( $m/z = 204$ ) and 6,7-dihydroxy-3,7-dimethyloctanal ( $m/z = 188$ ). The quantification of these by-products of the epoxidation of citronelal could not be done because only small amounts were present in the reaction mixture due to the formation of surface complexes [19].

The profile of the citral epoxidation is shown in Fig. 7. The major product of this reaction is the 6,7-epoxide (**3a**). The 2,3-epoxide (**3b**) and diepoxide (**3c**) were not obtained. In contrast to the citronelal epoxidation, the selectivity for the epoxide decreases rapidly from the beginning of the reaction. In fact, ESI-MS analysis at the end of the citral epoxidation detected 3,7-dimethyloctan-2,6-dienoic acid ( $m/z = 184$ ) and 3-methyl-5-(3,3-dimethyloxiran-2-yl)pent-2-enoic acid ( $m/z = 168$ ); however, as seen for citronelal, the quantification of these by-products was not possible as only small amounts were present on the reaction mixture due to the formation of surface complexes [19].

Although, the most nucleophilic part is the aldehyde group ( $-4.98\text{ eV}$ ), a higher selectivity for the 6,7-epoxide (**3a**) was obtained (ca. 60% selectivity after 5 h). The formation of the 2,3-epoxide (**3b**) and diepoxide (**3c**) was not observed as the carbon–carbon double bond at  $\text{C}_2\text{--C}_3$  is a poor nucleophile ( $-6.02\text{ eV}$ ), due to the electron density withdrawing effect of the carbonyl substituent on this alkene group (Fig. 8). On the other



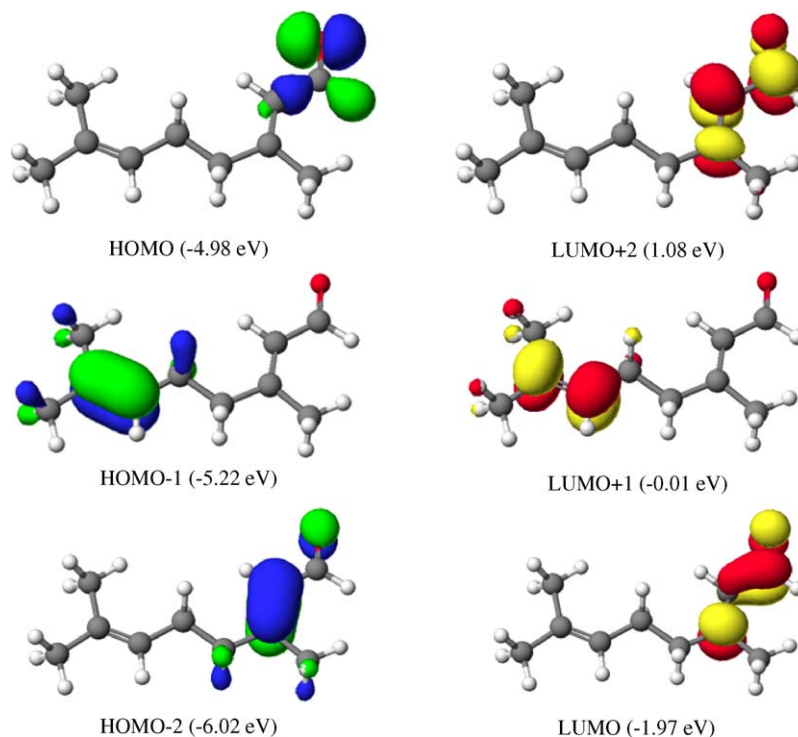


Fig. 8. Frontier molecular orbitals of citral.

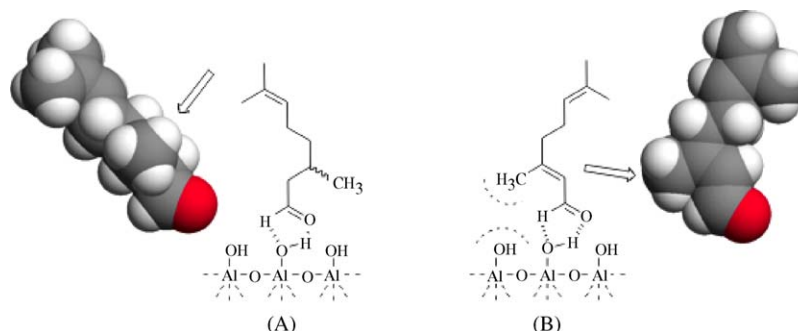


Fig. 9. Interaction of (A) citronelal and (B) citral with the alumina surface. The arrow indicates the methyl substituent in each molecule.

hand,  $\text{Al}_2\text{O}_3/\text{KF}$  has been shown to catalyze the epoxidation of the electron deficient carbon–carbon double bond of enones using anhydrous TBHP as oxidant [20,21].

The preference for epoxidation instead of the aldehyde oxidation, despite the higher energy of the lone electron pair of the aldehyde moiety ( $-4.98$  eV) compared with the carbon–carbon double bond at  $\text{C}_6$ – $\text{C}_7$  ( $-5.22$  eV), is probably also due to the interaction between the aldehyde group and the polar alumina surface ( $\text{Al-OH}$ ). As discussed for citronelal, this interaction can decrease the energy of this molecular orbital and consequently make this lone electron pair less nucleophilic. However, due to the higher steric hindrance of the methyl group at position 3 (Fig. 9B), this interaction of the aldehyde group and the alumina surface is less efficient for citral than for citronelal. For that reason, the selectivity for the epoxide decreases faster during the reaction for citral (Fig. 7) than for citronelal (Fig. 5).

Citronelol epoxidation (Fig. 10) using SG alumina and anhydrous 24 wt% hydrogen peroxide allowed a yield of 42% with

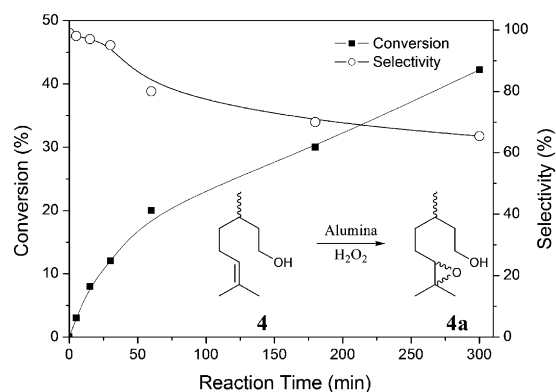


Fig. 10. Epoxidation of citronelol. Reaction conditions: 100 mg of SG alumina calcined at  $400^\circ\text{C}$ , 20 mmol of citronelol, 40 mmol of anhydrous  $\text{H}_2\text{O}_2$  24 wt%,  $80^\circ\text{C}$ .

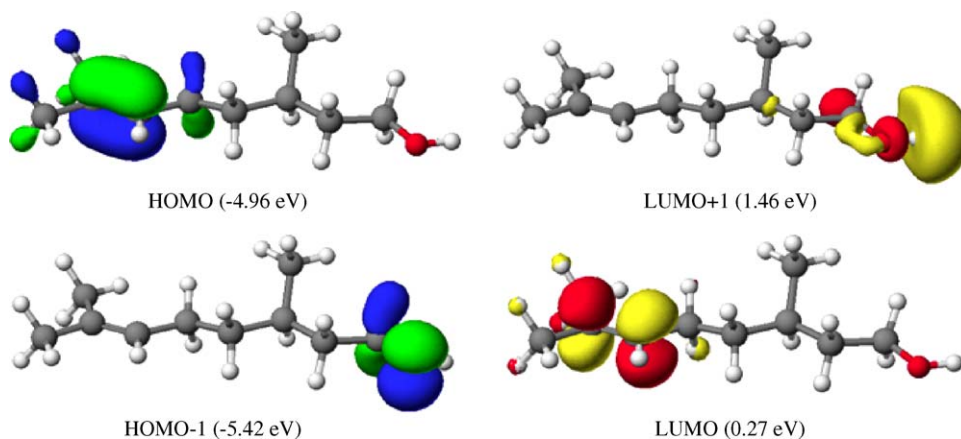


Fig. 11. Frontier molecular orbitals of citral.

a selectivity of 65% (Table 1, entry 8) for the 6,7-epoxides (**4a**). Surprisingly, the reaction using aqueous 70 wt% hydrogen peroxide showed a higher yield and a better selectivity for the 6,7-epoxides (47% and 73%, respectively; Table 1, entry 8), indicating that the presence of water avoids oligomerization or further oxidation of the alcohol moiety. In these reactions, using either aqueous or anhydrous  $\text{H}_2\text{O}_2$ , 1,6,7-triol was not observed by ESI-MS.

Also for citral the preferred oxidation takes place at the most nucleophilic functionality of the molecule (Fig. 11). The oxidation of the alcohol group is disfavoured as the energy of this molecular orbital is very low ( $-5.42$  eV) compared to the carbon–carbon double bond ( $-4.96$  eV). This should be the reason that a high preference for epoxidation instead of oxidation of the alcohol group is also observed when using a highly active catalyst such as methyltrioxorhenium [16,22,23].

The epoxidation of (1*S*)- $\alpha$ -pinene (Fig. 12) leads to the preferential formation, with ca. 60% selectivity, of the epoxide **5a** (entry 10) with moderate yield (32%). Higher yields and selectivities could be achieved when continuous azeotropic distillation was used to remove water from the reaction mixture [9]. However, as we were interested to determine the reactivity of this terpene under very demanding conditions, we preferred

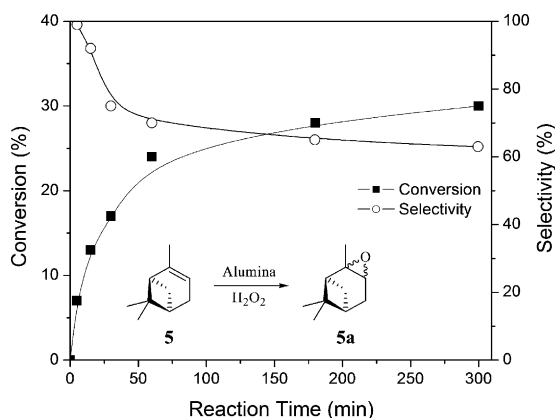
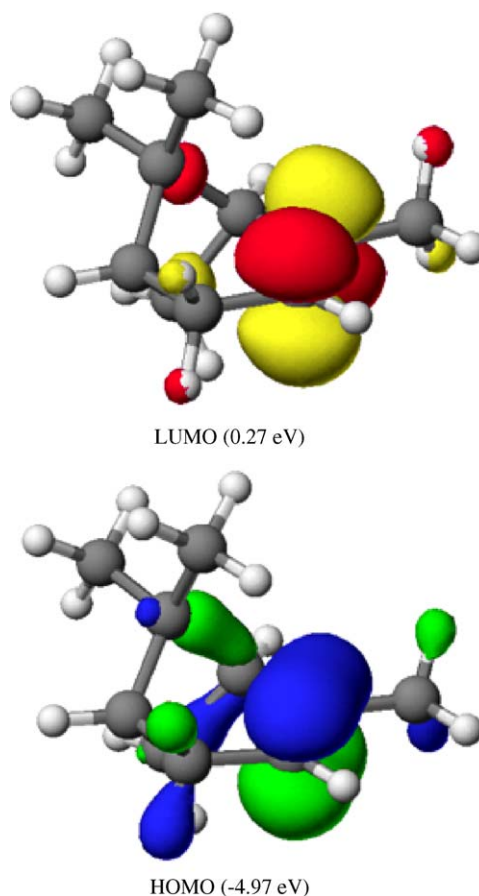


Fig. 12. Epoxidation of (1*S*)- $\alpha$ -pinene. Reaction conditions: 100 mg of SG alumina calcined at  $400^\circ\text{C}$ , 20 mmol of linalool, 40 mmol of anhydrous  $\text{H}_2\text{O}_2$  24 wt%,  $80^\circ\text{C}$ .

not to use azeotropic distillation for the removal of water, as it would mask our analysis. The presence of  $\alpha$ -camphoric aldehyde and 2,6,6-trimethylbicyclo[3.1.1]heptane-2,3-diol in the reaction mixture was detected by ESI-MS analysis, showing that the acid catalyzed rearrangement and the solvolysis of the epoxide also takes place on the alumina surface.

It is interesting to see that the HOMO of  $\alpha$ -pinene (Fig. 13) is very delocalized over the molecule. This means that other reactions can take place that do not involve the carbon–carbon

Fig. 13. Frontier molecular orbitals of (1*S*)- $\alpha$ -pinene.

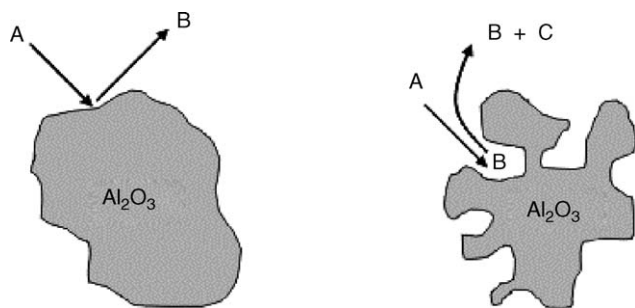


Fig. 14. Non-porous and porous alumina for catalytic epoxidation of olefins.

double bond. For example, oligomerization and rearrangements are also prone to occur.

The system ( $\text{Al}_2\text{O}_3/\text{H}_2\text{O}_2$ ) used for the epoxidation of terpenes gave good site- and chemo-selectivity. Products from the oxidation of the alcohol groups, present in both linalool and citronellol, were not detected and oxidation products from the aldehyde groups, present in citronelal and citral, were only detected in minor amounts. This makes the present system comparable to others reported in the literature [24,25], but with the advantage that the catalyst used is solid (allowing easy recycling), inexpensive and does not require any co-catalyst.

It is important to realize that for anhydrous hydrogen peroxide SG alumina showed a higher selectivity for epoxides than commercial neutral chromatographic alumina, as the conversion of terpenes was usually higher using sol–gel alumina and the selectivity also remained higher during the reactions when anhydrous hydrogen peroxide was used. This fact is related to the textural properties of aluminas. SG alumina has no structural porosity [11,17] while commercial chromatographic alumina has ink-bottle like shaped pores [11]. As the products of the oxidation (B) are always more polar than the reagents (A), a stronger interaction between the products and the catalytic surface is expected. For porous materials, the residence time inside these pores can be sufficiently long for further oxidation or ring-opening reactions, resulting in the formation of by-products (C) and decreasing the selectivity for epoxides (Fig. 14).

#### 4. Conclusions

- (1) SG alumina allowed higher conversions with better selectivity for terpene epoxides. The reasons for such better catalytic performance has already been discussed in our earlier reports [17,18] and is related to the suitable hydrophilicity, acidity and textural properties of the SG alumina surface for oxidative transformations.
- (2) The oxidations of terpenes showed good site- and chemo-selectivity giving monoepoxides as the major products. The selectivity for epoxides can be enhanced when continuous azeotropic distillation is used to remove the water from the reaction mixture [9]. However, we did not use this artifice

in order to have a real analysis of the chemical reactivity of these terpenes and their epoxides under reaction conditions.

- (3) The selectivity for epoxides could be understood through electronic structure calculations, which showed that the most nucleophilic group of each terpene is predominantly epoxidized. This fact indicates that the oxygen transferred to the olefin acts as an electrophile.

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