

Alumina as heterogeneous catalyst for the regioselective epoxidation of terpenic diolefins with hydrogen peroxide

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Abstract

The epoxidation of several terpenic diolefins (carvone, limonene, terpinolene, α -terpinene and γ -terpinene) in anhydrous conditions using alumina as a heterogeneous catalyst and hydrogen peroxide as the oxidant agent is studied in this work. Several kinds of chromatographic aluminas have been employed (acidic, basic and neutral), in order to study the effect of the surface acidity on the reaction. The reusability of the catalyst has also been addressed. Basic alumina was the catalyst that gave better activity and selectivity. The reactivity of the substrate increases with the nucleophilic character of its double bonds, and the regioselectivity to some monoepoxides is also related to this nucleophilic character. The epoxidation rate of carvone, limonene and terpinolene increased with the alumina/terpene molar ratio. The selectivity to epoxides increased for carvone, and it passed through a maximum for limonene and terpinolene with this variable. From the comparison between experiments performed removing the catalyst, without removing it, and without catalyst, it was deduced that alumina is responsible for the high activity and selectivity obtained when it is added to the reaction medium, and that a heterogeneous epoxidation occurs on alumina surface. The study of the reusability of alumina in the epoxidation of limonene and terpinolene shows negligible changes on selectivity after several cycles, whereas the decrease of activity in successive cycles is significant for the long reaction times used in limonene epoxidation.

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1. Introduction

Epoxides are important intermediates in organic synthesis due to the high reactivity of the oxirane ring in their structure, from which a wide variety of functional groups can be obtained. The epoxides of terpenes are particularly important because these epoxides are an important building block for natural products synthesis [1–3], and limonene 1,2-epoxide is a promising monomer for the synthesis of a new biodegradable “polylimonene carbonate” from biorenewable resources [4]. In the last decade, the development of the so-called “green processes”, which are proposed as an alternative to other routes, reducing the environmental impact and the amount of by-products, has aroused great interest [5]. This development generally implies the use of heterogeneous and selective catalysts,

as the separation and recovery of the catalyst and the desired products is easier. As far as the oxidation reaction is concerned, the use of hydrogen peroxide as the oxidant agent offers several advantages: (i) it is relatively cheap and (ii) it is environmentally friendly as water is obtained as the by-product. One heterogeneous catalyst with widespread use in organic synthesis is alumina, used both as catalyst and as support for active metals [6–9]. Among all the different polymorphs of alumina, gamma-alumina is the one most used as catalyst, having high surface area and a pore size distribution with a high proportion of mesopores [10]. In 1977, the capability of alumina of producing intermediates with oxidant character in the presence of hydrogen peroxide was discovered [11]. In the following years Rebek and McCready [12] observed that these intermediates could epoxidize olefins, but obtaining low substrate conversions for high catalyst to substrate ratios. Recently, it was discovered that using anhydrous hydrogen peroxide as oxidant agent and ethyl acetate as solvent for this kind of reactions results in a significant improvement in the activity of the catalyst

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[13]. The catalytic properties of different kinds of alumina in the epoxidation reaction of several alkenes, such as cyclohexene, cyclo-octene and styrene has also been studied [14–16], but there is little information published about regioselective epoxidation of diolefins. The use of alumina as heterogeneous catalyst offers several advantages with respect to other systems with supported active metals: (i) it is available commercially, (ii) it has a relatively low cost, and (iii) the problem of metal lixiviation to solvent does not exist. Here, we have analysed the catalytic activity of alumina in the regioselective epoxidation of several terpenic diolefins (carvone, limonene, terpinolene, α -terpinene and γ -terpinene). Several kinds of chromatographic aluminas have been employed (acidic, basic and neutral), in order to study the effect of the surface acidity on the reaction. The reusability of the catalyst has also been addressed.

2. Experimental

Chromatographic aluminas were supplied by Aldrich (acidic, basic and neutral). These catalysts were characterized with the following techniques:

- XRD (Siemens D5000) using Cu K α radiation over the 2θ range from 5 to 80, with step size of 0.05° and counting times of 1 s.
- Nitrogen adsorption–desorption measurements at 77 K (Micrometrics ASAP 2010). Surface areas were determined with the BET method and pore volume and pore size distribution were calculated using the BJH method.

Carvone (5-isopropenyl-2-methyl-2-cyclohexenone, 98%), limonene (4-isopropenyl-1-methyl-1-cyclohexene, 99%), α -terpinene (1-isopropyl-4-methyl-1,3-cyclohexadiene, 85%) and γ -terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene, 97%) were supplied by Aldrich. Terpinolene (4-isopropylidene-1-

methylcyclohexene, 85%) was supplied by Fluka. All the substrates were used without further purification. The substrates and their respective mono- and diepoxides are shown in Fig. 1.

Solutions of anhydrous hydrogen peroxide in dry ethyl acetate were prepared by liquid–liquid extraction from a commercial hydrogen peroxide aqueous solution (Aldrich, 50%, w/w), and removing the water using anhydrous sodium sulphate as desiccant. Hydrogen peroxide concentration in ethyl acetate solutions was determined by mixing a sample (previously diluted with water) with TiOSO₄ and measuring the resulting yellow peroxy-complex concentration by UV–vis spectrophotometry [17]. The mean hydrogen peroxide concentration in ethyl acetate obtained with this method was 10%.

In a typical experiment, 0.25 g of the catalyst (previously dried at 110 °C) were added to a mixture of 10 mmol of substrate, 20 mmol of hydrogen peroxide (~10% in ethyl acetate) and 30 ml of ethyl acetate dry (substrate:H₂O₂:Al₂O₃ molar ratio was 4:8:1). The epoxidation reaction was carried out in a magnetically stirred two necked vessel fitted with a reflux condenser heated in an oil bath at 60 °C. Reaction time was 72 h (except otherwise indicated), starting from the moment alumina was added to the mixture. The evolution of the concentration of substrate and reaction products was monitored by taking samples from the reaction mixture at different times, and analysing them by GC–MS (Agilent Technologies 6890N GC equipped with an J&W DB-23 capillary column and 5973N mass selective detector). The evolution of hydrogen peroxide concentration was monitored using the method described previously.

Several parameters were calculated to evaluate the catalyst performance, defined as follows:

$$\text{Conversion (\%)} = 100 \left(1 - \frac{\text{remaining diolefin}}{\text{initial diolefin}} \right)$$

$$\text{H}_2\text{O}_2 \text{ consumption (\%)} = 100 \left(1 - \frac{\text{remaining peroxide}}{\text{initial peroxide}} \right)$$

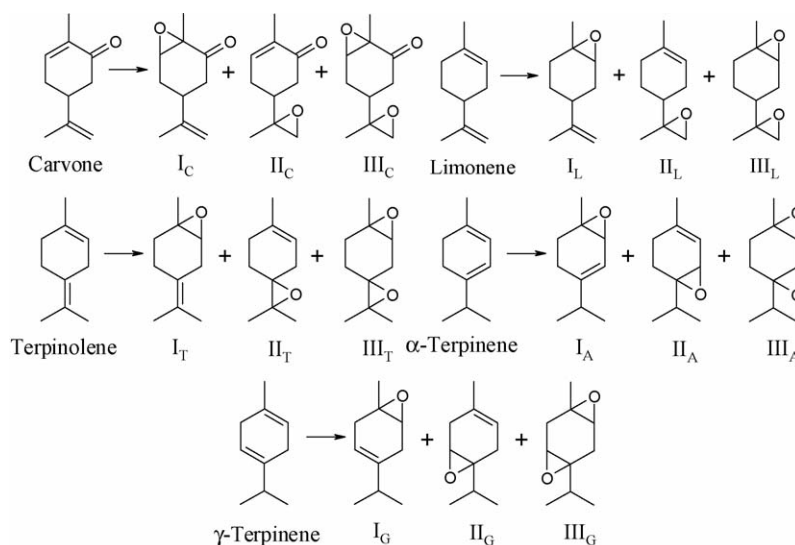


Fig. 1. Substrates and their respective monoepoxides and diepoxides.

Table 1
Textural properties of the aluminas studied

Alumina character	BET area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	pH in aqueous suspension
Basic	161	0.26	4.8	9.5 ± 0.5
Neutral	172	0.26	4.5	7 ± 0.5
Acidic	190	0.28	4.1	4.5 ± 0.5

$$\text{Products selectivity (\%)} = 100 \left(\frac{\text{product}}{\sum \text{products}} \right)$$

$$\text{H}_2\text{O}_2 \text{ efficiency (\%)} = 100 \left(\frac{\text{mmol epoxides}}{\text{mmol of H}_2\text{O}_2 \text{ consumed}} \right)$$

3. Results and discussion

3.1. Characterization of the catalysts

The XRD spectra of all the aluminas used in this work showed that they are of the γ -type, since the XRD patterns are coincident with the ones available in the literature for this polymorph of alumina [7]. The textural properties of these materials determined by nitrogen adsorption analysis are shown in Table 1. The pH of each alumina in aqueous suspension is also given in this table.

It is observed that all the aluminas have similar values of the BET surface area, pore volume and average pore diameter, although a slight increase in the BET surface area and the pore volume with surface acidity, and a slight decrease of the average pore diameter, is also noticed.

3.2. Effect of surface acidity of alumina

The effect of surface acidity of alumina on its catalytic activity was studied for the epoxidation of carvone and limonene, the results being shown in Fig. 2a. In order to compare the catalytic

Table 2
Catalytic activity of alumina in the epoxidation of limonene with different solvents

Solvent ^a	Conversion (%)	Products selectivity (%)			
		I _L	II _L	III _L	Others
Ethyl acetate	77.6	81.0	6.5	9.4	3.1
Methanol	17.2	31.2	7.7	–	61.1
Propanol	31.6	46.0	8.7	–	45.3
Acetonitrile	34.1	57.9	9.4	1.7	31.0
Tetrahydrofuran	26.1	31.4	6.2	–	62.4

^a Reaction conditions: 10 mmol substrate, 20 mmol H₂O₂, 30 ml of ethyl acetate or 36 ml of other solvent, 0.25 g Al₂O₃, 60 °C, 72 h.

activity of the different aluminas taking into account the effect of the surface area of the solid, the activity is expressed as mmol of total epoxides per m² of surface area. The lower activity of alumina for the epoxidation of carvone as compared to limonene is due to the lower reactivity of the terminal alkene in carvone, as it is discussed later. For carvone, only monoepoxides were observed, so only the selectivity to these products is considered.

It is observed that the surface acidity affects negatively the activity and selectivity of alumina as catalyst, which can be attributed to higher affinity to water of acidic alumina [18], leading to a higher blockage of its surface sites.

Fig. 2b shows the effect of the addition of water (30 mmol) on the activity and selectivity obtained with basic and acidic alumina. It is observed that both activity and selectivity decrease for both kinds of alumina.

In view of these results, the rest of experiments, discussed in the next sections, were carried out with basic alumina.

3.3. Effect of water excess using solvents miscible with water

To confirm the negative effect caused by the excess of water in the reaction medium, different experiments have been carried out using aqueous hydrogen peroxide (33%, w/v) in several

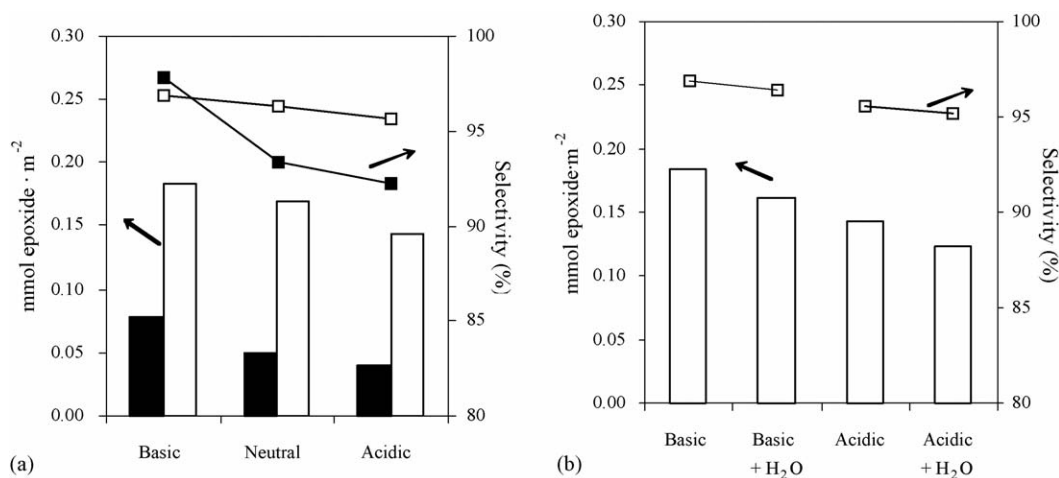


Fig. 2. Effect of surface acidity on the catalytic activity of alumina in the epoxidation of carvone and limonene. Reaction conditions: 10 mmol substrate, 20 mmol H₂O₂, 30 ml AcOEt, 0.25 g Al₂O₃ (substrate/H₂O₂/Al₂O₃ = 4/8/1), 0 or 30 mmol H₂O, 60 °C, 72 h. The activity is expressed as mmol of total epoxides per m² of surface area. Black bars, carvone; white bars, limonene. (■) Selectivity to monoepoxides of carvone; (□) selectivity to mono- and diepoxides of limonene. (a) Carvone and limonene. (b) Limonene with and without water.

Table 3
Catalytic activity of alumina in the epoxidation of terpenic diolefins

Substrate ^a	Conversion (%)		H ₂ O ₂ (%)		Products selectivity (%)				
	With catalyst	Without catalyst	Consumed	Efficiency	I	II	III	<i>p</i> -Cymene	Others
Carvone	8.7	0.8	9.1	48	3.6	93.8	–	–	2.6
Limonene	31.3	1.2	22.4	69	84.9	9.9	2.0	–	3.2
γ -Terpinene	37.1	22.5	19.2	61	33.5	33.5	1.8	27.5	3.7
Terpinolene	48.1	25.0	24.7	83	4.6	75.4	2.1	4.3	13.6
α -Terpinene	56.4	21.8	28.3	20	8.2	11.6	–	39.3	40.9

^a Reaction conditions: 10 mmol substrate, 20 mmol H₂O₂, 30 ml AcOEt, 0 or 0.25 g Al₂O₃, 60 °C, 8 h.

solvents miscible with water. Results are shown in Table 2. It is observed that water has a negative influence producing an important decrease of conversion and selectivity. These results indicate that the anhydrous environment, obtained with dry ethyl acetate, is necessary to obtain good results with this catalytic system.

3.4. Epoxidation reactions

Table 3 shows the catalytic activity of alumina in the epoxidation of the terpenic diolefins studied in this work. The results obtained in a blank experiment without catalyst are also included in this table.

The conversion values indicate that the reaction rate increases with the nucleophilic character of the alkene groups in the molecule, which increases with the number of electron donor substituents. The effect of the number of alkyl groups adjacent to the two double bonds present in each molecule is shown in Fig. 3. It is also observed that the blank experiments (see Table 3) give relatively high conversion of γ -terpinene, terpinolene and α -terpinene. This behaviour is attributed to the high reactivity of the exocyclic double bond of terpinolene and the high stability of the benzenic derivatives resulting from both terpinenes. For these substrates, it was observed that atmospheric oxygen acts as an oxidant agent competing with hydrogen peroxide. An experiment performed with terpinolene under inert atmosphere resulted in a conversion similar to the one obtained in the blank experiment obtained with carvone and limonene.

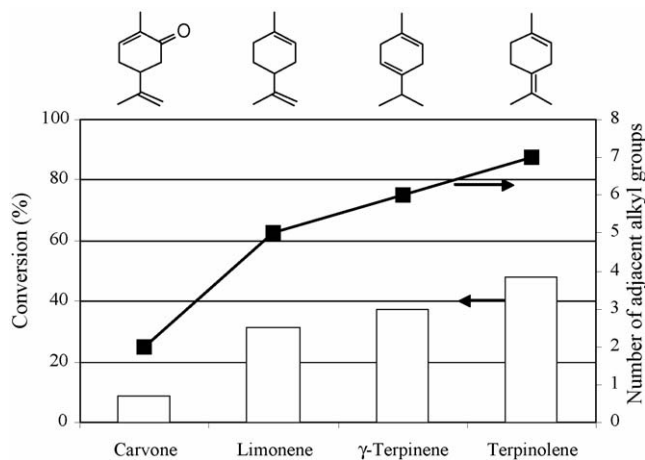


Fig. 3. Effect of the number of alkyl groups adjacent to the two double bonds on conversion in the epoxidation of terpenic diolefins with alumina. Reaction conditions in Table 3.

The nucleophilic character also increases when there exist conjugation between the two double bonds in the molecule, which explains the higher reactivity of α -terpinene (Table 3). For carvone, the reactivity of the endocyclic double bond is quite low due to the electronic-withdrawing effect of the ketone group conjugated with this double bond, giving the exocyclic monoepoxide (II_C) as the main product by means of a regioselective epoxidation. The regioselectivity observed in the epoxidation of limonene and terpinolene can be attributed to the effect of the number of substituents in each double bond present in the molecule. For limonene, the endocyclic monoepoxide (I_L) is the most abundant product, which comes from the epoxidation of the more substituted double bond. The same applies to the exocyclic monoepoxide of terpinolene. The two double bonds of α - and γ -terpinene have the same number of substituents. For this reason, the epoxidation of these substrates did not show regioselectivity and the selectivities to the monoepoxides of α - and γ -terpinene are similar. For α -terpinene, a high amount of by-products is obtained, resulting in a low selectivity to the epoxides, which can be related to the high reactivity of this substrate. In the epoxidation of α - and γ -terpinene, it is observed that a significant amount of *p*-cymene is obtained as by-product, which is probably produced by oxidative dehydrogenation reactions [19] involving the internal double bonds in the six-member ring. This compound has great commercial interest as a precursor for *p*-cresol [20], increasing the economic value of the products.

In Table 3, it is also observed that the H₂O₂ efficiency increases with the reactivity of the substrate. However, for α - and γ -terpinene, the efficiency is lower than expected if this trend is considered, which is due to the formation of by-products, mainly *p*-cymene, attributable to the high reactivity of these substrates. For them, and for terpinolene, it was observed that all the H₂O₂ consumed was used up in the formation of products, with negligible oxygen production.

3.5. Effect of alumina loading on the epoxidation of terpenes and H₂O₂ decomposition

The effect of alumina loading on conversion, selectivity and H₂O₂ efficiency for the epoxidation of carvone, limonene and terpinolene is shown in Fig. 4.

Fig. 4a shows that, as expected, the increase in the alumina/substrate ratio results in higher conversions for the three substrates. It must be noted that epoxidation of all the substrates occurs in the absence of alumina, although with

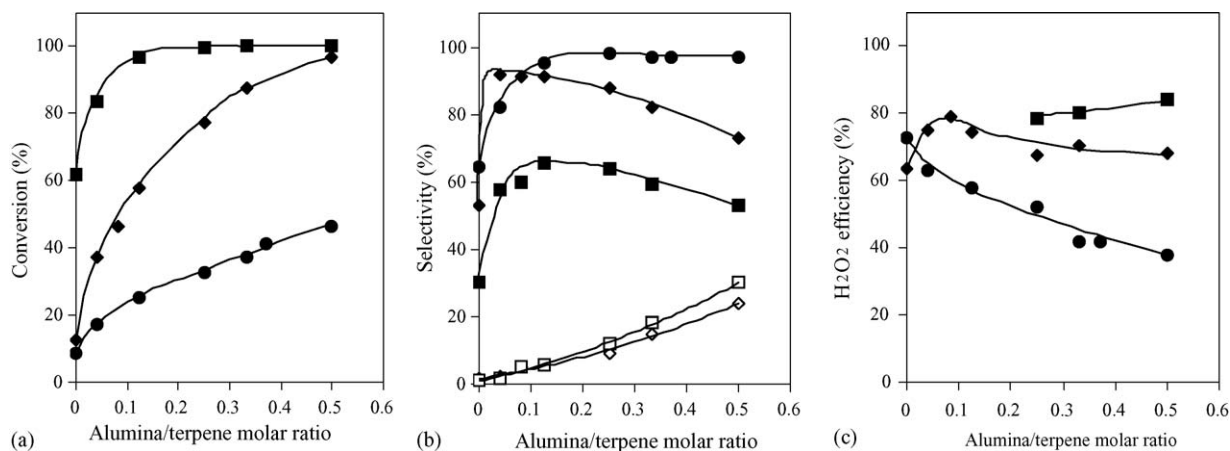


Fig. 4. Effect of alumina loading on conversion, selectivity and H₂O₂ efficiency for the epoxidation of carvone, limonene and terpinolene. Reaction conditions: 10 mmol substrate, 20 mmol H₂O₂, 30 ml AcOEt, 0–0.5 g Al₂O₃, 60 °C, 72 h. (a) Effect on conversion: (●) carvone; (◆) limonene; (■) terpinolene. (b) Effect on selectivity: (●) selectivity to II_C; (◆) I_L; (■) II_T; (◇) III_L; (□) III_T. (c) Effect on H₂O₂ efficiency: (●) carvone; (◆) limonene; (■) terpinolene.

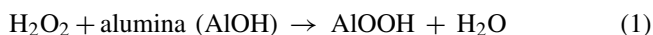
much lower conversion and selectivity. This reaction is called “homogeneous epoxidation” from this point on. For terpinolene complete conversion is obtained with alumina/terpene molar ratios higher than 0.1. The observed reactivity order (terpinolene > limonene > carvone) can be explained in terms of the nucleophilic character of the double bonds in the molecule, which has already been discussed in the previous section.

The dependence of selectivity to the monoepoxides on alumina/terpene ratio (Fig. 4b) is different for the three substrates. The selectivity to II_C increases with this parameter for carvone, whereas it goes through a maximum for the endocyclic epoxide of limonene (I_L) and the exocyclic epoxide of terpinolene (II_T). This different behaviour can be explained considering two simultaneous effects, the effect of alumina loading on the ratio between the reaction rates of heterogeneous and homogeneous epoxidation, and the effect of this variable on the formation of diepoxides. The higher is the alumina loading, the higher is the ratio between heterogeneous and homogenous epoxidation rates, but the rate of formation of diepoxides is higher too. For carvone, the formation of the diepoxide is not important because of the conjugation of the internal double bond with the ketone group, which reduces its nucleophilic character. Thus, the dominating effect of increasing the alumina loading is the improvement of selectivity due to the higher reaction rate of heterogeneous epoxidation. For limonene and terpinolene, this effect is much stronger for low alumina/terpene ratios. However, for these substrates, when the alumina loading is increased, so does the rate of formation of diepoxides, as it shown in Fig. 4b, which reduces the selectivity to monoepoxides, explaining the presence of a maximum.

Fig. 4c shows that the dependence of H₂O₂ efficiency on the alumina/terpene molar ratio is also different for the three substrates. The H₂O₂ efficiency increases with this parameter for terpinolene, it goes through a maximum for limonene, and it decreases for carvone. It must be reminded that this efficiency has been defined as the number of mmoles of epoxides obtained per mmol of H₂O₂ consumed.

This behaviour can be explained considering the following simplified scheme of reactions occurring between hydrogen peroxide, alumina and substrate:

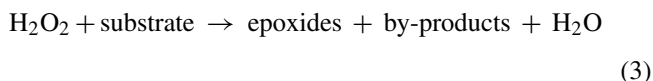
- Formation of active species:



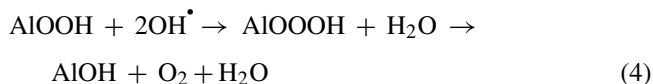
- Heterogeneous epoxidation:



- Homogeneous epoxidation:



- Decomposition of active species:



The mechanism of decomposition of AlOOH species has been proposed elsewhere [11]. The hydroxyl radicals are formed either by homolysis of the AlOOH groups, or by reaction of H₂O₂ with Fe impurities present in alumina (0.02% maximum, according to supplier’s specifications).

For terpinolene, due to its high reactivity, the rate of epoxidation is much higher than the rate of decomposition of active species. It was observed that for alumina/terpene molar ratio higher than 0.25, all the hydrogen peroxide that it is consumed in reactions (1) and (3) leads to epoxides and by-products (reactions (2) and (3)) in this case. Therefore, the H₂O₂ efficiency increases with alumina loading because so does the rate of heterogeneous epoxidation, which is selective to epoxides. However, for ratios lower than 0.25, and only for terpinolene, it was observed that atmospheric oxygen acts as oxidant agent competing with hydrogen peroxide. As a result, efficiencies of H₂O₂ higher than 100% were obtained, which have not been included in Fig. 4c. This behaviour is attributed to the high reactivity of the exocyclic double bond of terpinolene.

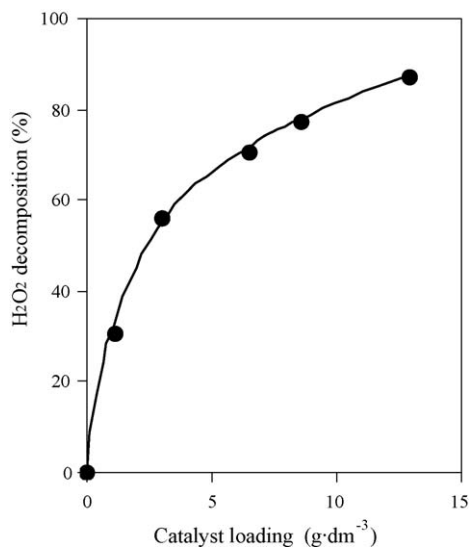


Fig. 5. Effect of alumina loading on H₂O₂ decomposition. Reaction conditions as in Fig. 4, without substrate.

For limonene, the heterogeneous epoxidation and the decomposition of active species have similar importance. At low alumina loadings, the H₂O₂ efficiency increases with this parameter because the ratio between heterogeneous and homogenous epoxidation rates increases. At higher alumina loadings, a higher amount of active species is formed, so the probability of undergoing a decomposition process increases.

The increase in the reaction rate between alumina and hydrogen peroxide (reaction (1)) with alumina loading has been observed experimentally, as it is shown in Fig. 5. This effect reduces the H₂O₂ efficiency, explaining the presence of a maximum. For carvone, its low reactivity makes the effect of the heterogeneous epoxidation rate less important. The dominating effect is the increase of the amount of active species with alumina loading, so that the H₂O₂ efficiency is reduced, as it has been explained before.

3.6. Study of the heterogeneous character of alumina as catalyst

An experiment was performed with terpinolene, because of its high reactivity, in order to confirm that alumina acts as a truly heterogeneous catalyst, removing the catalyst by filtration at an intermediate point of the reaction (4 h). The effect of this removal on conversion and selectivity to the monoepoxide II_T is shown in Fig. 6, where the evolution of conversion and selectivity in this experiment is compared with the ones obtained without alumina removal and in a blank experiment without alumina.

It is observed that there is noticeable decrease of the reaction rate from the moment alumina is removed onwards, approaching the one corresponding to the homogeneous epoxidation occurring in the blank experiment. A decrease of the selectivity is also observed. From these results, it is deduced that alumina is responsible for the high activity and selectivity obtained when it is added to the reaction medium, and that a heterogeneous epoxidation occurs on alumina surface. It also deduced that leaching of active species is not important.

3.7. Study of the reusability of alumina

The reusability of alumina as catalyst was studied for the epoxidation of terpinolene and limonene, which were selected to take into account the effect of different reaction times on the reusability. The catalyst was recovered of the reaction mixture by filtration after 8 h of reaction for terpinolene, and after 72 h for limonene. Afterwards, it was washed with ethyl acetate, dried at 110 °C overnight, and then, calcined at 500 °C for 5 h. An experiment performed with the catalyst reused directly without calcination resulted in lower conversion than the one obtained with calcinations. The recovered catalyst was then used in a new epoxidation experiment with the same conditions. The effect of three cycles on conversion and selectivity to I_L (limonene) and II_T (terpinolene) is shown in Fig. 7.

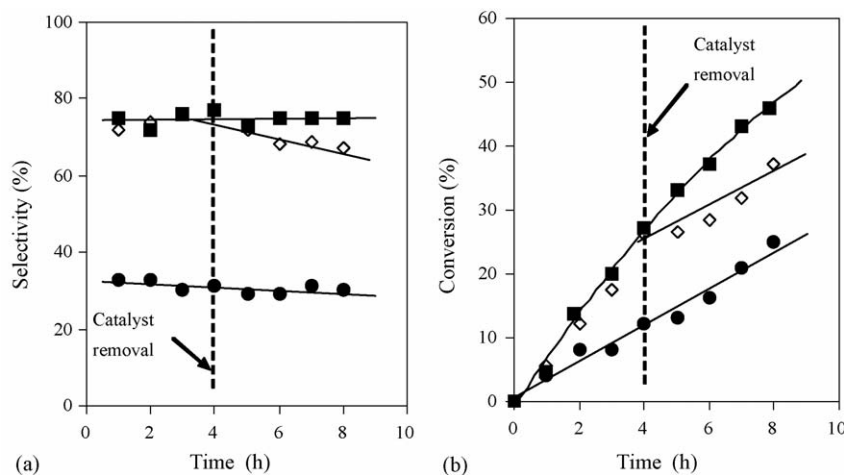


Fig. 6. Comparison of the conversion and selectivity to exocyclic monoepoxide (II_T) for the epoxidation of terpinolene with and without catalyst removal, and in a blank experiment without alumina. Reaction conditions in Table 1. (■) Without catalyst removal; (◇) with catalyst removal; (●) blank experiment without alumina. (a) Selectivity; (b) conversion.

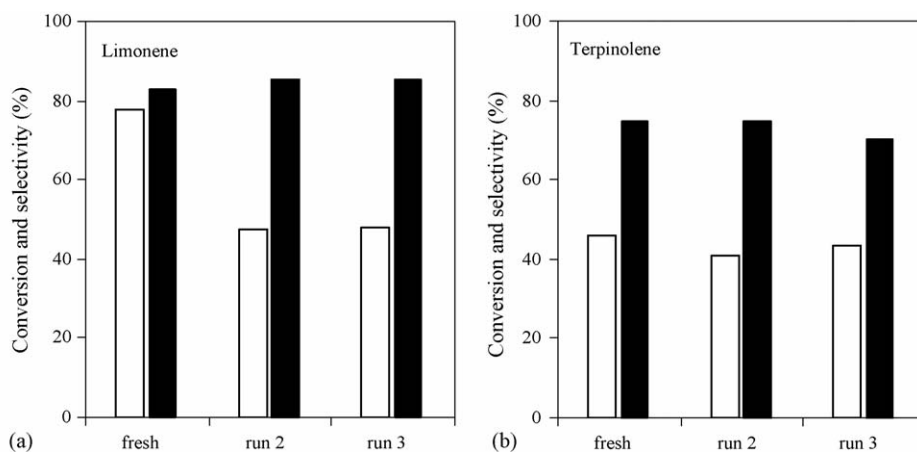


Fig. 7. Effect of successive reuses of alumina in the epoxidation of limonene and terpinolene on conversion and selectivity to I_L (limonene) and to II_T (terpinolene). Reaction conditions in Fig. 2 for limonene and Table 3 for terpinolene. White bars, conversion; black bars, selectivity. (a) Limonene; (b) terpinolene.

From these results, it is observed that there is no significant decrease of selectivity in the successive reuses of alumina. However, the activity of alumina decreases significantly for the long reaction times used in limonene epoxidation. This deactivation of alumina is attributed to a change in the active centers during long reaction times. Surface area, pore volume and average pore diameter increased after the calcination of the used catalyst (from 161 to 230 $m^2 g^{-1}$, from 0.26 to 0.39 $cm^3 g^{-1}$ and from 4.8 to 5.4 nm, respectively). However, this increase was the same as the one obtained with the fresh catalyst. The fresh catalyst used with and without previous calcination showed very similar performance. For this reason, the loss of activity is attributed to a changes in the active centres and not to the variation of textural properties.

4. Conclusions

In this work, the catalytic activity of alumina in the regioselective epoxidation of several terpenic diolefins (carvone, limonene, terpinolene, α -terpinene and γ -terpinene) was studied. After comparing the performance of basic, neutral and acid alumina in the epoxidation of carvone and limonene, it was observed that basic alumina gave the best results of both conversion and selectivity for both substrates. The study of the epoxidation of the different substrates with basic alumina showed that the reaction rate increases with the nucleophilic character of the alkene groups in the molecule. The regioselectivity observed in the epoxidation of carvone, limonene and terpinolene can also explained in terms of differences in the nucleophilic character of the double bonds present in each molecule. The epoxidation rate of carvone, limonene and terpinolene increased with the alumina/terpene molar ratio. The selectivity increased for carvone, and it passed through a maximum for limonene and terpinolene with this variable. This different behaviour can be explained considering two simultaneous effects, the effect of alumina loading on the ratio between the reaction rates of heterogeneous and homogeneous epoxidation, and the effect of this variable on the formation of diepoxides. The variation of the H_2O_2 efficiency with alumina loading depends on the relative importance of the

rates of epoxidation of the substrate and decomposition of the active species.

From the comparison between experiments performed removing the catalyst, without removing it, and without catalyst, it was deduced that alumina is responsible for the high activity and selectivity obtained when it is added to the reaction medium, and that a heterogeneous epoxidation occurs on alumina surface. The study of the reusability of alumina in the epoxidation of limonene and terpinolene showed that selectivity remains practically constant after several cycles, whereas the decrease of activity in successive cycles is significant for the long reaction times used in limonene epoxidation.

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