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## Short Communication

# A novel Fe(III) salt-catalyzed monoterpene aerobic oxidation in methyl alcohol



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### 1. Introduction

Monoterpenes are natural olefins which constitute an abundant raw material, whose oxygenate derivatives are the ingredients of fragrances, drug synthesis intermediates, and fine chemical industries [1]. Olefin oxidation reactions are interesting from the viewpoint of industry, especially when dioxygen is employed, an environmentally benign oxidant that produces water as its only by-product [2]. Nevertheless, the use of dioxygen requires a transition metal catalyst for its activation, which generally requires special conditions to work, such as the presence of stabilizing ligands or reversible reoxidants [3,4].

The use of Pd(II) catalysts in olefin aerobic oxidation has been comprehensively explored, because the reaction generally involves  $\sigma$  or  $\pi$ -organopalladium intermediates instead of radical species, which make selectivity control difficult [5]. An example is the Wacker process, which is used on an industrial scale to oxidize C<sub>2</sub>H<sub>4</sub> into CH<sub>3</sub>CHO (PdCl<sub>2</sub>/CuCl<sub>2</sub>/O<sub>2</sub>) [6]. However, the Wacker catalyst is only ineffective in the monoterpene oxidation reactions, due to the formation of chlorinated products and the high Lewis acidity of CuCl<sub>2</sub> [7]. Several modifications in the Wacker system have been proposed, such as replacing the CuCl<sub>2</sub> by other reoxidant [8]. In this regard, we developed a catalytic system based on a nitrate reoxidant (i.e., Pd(OAc)<sub>2</sub>/M(NO<sub>3</sub>)<sub>n</sub> (M = Li(1), Cu(II) or Fe(III); n = 1, 2 or 3), which was employed in Pd(II)-catalyzed monoterpene oxidation by dioxygen [9]. In that work, the Fe(NO<sub>3</sub>)<sub>3</sub> was used exclusively as a palladium reoxidant; no catalytic action was reported [10]. Actually, the use of iron as a catalyst in

### ABSTRACT

The Fe(III)-catalyzed aerobic oxidation of monoterpenes in CH<sub>3</sub>OH has been developed, in which simple Fe(III) salts are used as catalysts in the absence of stabilizing ligands. Remarkably, Fe(NO<sub>3</sub>)<sub>3</sub> catalyst efficiently promotes the oxidation of monoterpenes under air or dioxygen. The highest TON and TOF reached 476 and 162 h<sup>-1</sup>, respectively. In general, reactions with 1.0–9.0 mol% of catalyst reached high conversions (ca. 90–99%) and high oxidation products selectivity (ca. 80%). Notably,  $\alpha$ -pinene and  $\beta$ -pinene were selectively oxidized into only allylic product, myrtenol methyl ether. The significant breakthroughs of this simple oxidative process are the use of inexpensive Fe(III) salts as catalysts and environmentally-friendly oxidants (air or dioxygen).

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monoterpene oxidation reactions by dioxygen has always involved nitrogen ligands. Transition metal porphyrin complexes and ironbipyridine complexes were also employed in monoterpene oxidation under a continuous flow of dioxygen [11–13]. However, in addition to the laborious synthesis of porphyrin complexes, most of these reactions use  $H_2O_2$  as stoichiometric oxidant [14].

In this paper, Fe(III)-catalyzed aerobic monoterpene oxidation reactions were performed using air or dioxygen in CH<sub>3</sub>OH, in the absence of bulkier nitrogen ligands. While we were assessing the catalytic activity of the Pd(OAc)<sub>2</sub>/Fe(NO<sub>3</sub>)<sub>3</sub> catalyst in oxidation of  $\beta$ -pinene by dioxygen, we found an unexpected result: the Fe(NO<sub>3</sub>)<sub>3</sub> was an active and selective catalyst; it promoted monoterpene oxidation, even in the absence of palladium. The main reaction parameters, such as temperature, nature and catalyst concentration and gas phase were addressed. High TONs were obtained and  $\alpha$  and  $\beta$ -pinenes were almost completely oxidized, with selectivity for myrtenol methyl ether equal to 60%.

### 2. Experimental procedures

### 2.1. Materials

All chemicals were purchased from commercial sources.  $Pd(OAc)_2$  (99.9% w/w),  $Cu(NO_3)_2 \cdot 6 H_2O$  (99% w/w) and  $Fe(NO_3)_3 \cdot 9 \cdot H_2O$  (99. 9% w/w) were acquired from Sigma-Aldrich.  $Fe_2(SO_4)_3 \cdot 5 H_2O$  (97% w/w) and  $LiNO_3 \cdot H_2O$  (99% w/w) were purchased from Merck.  $FeCl_3 \cdot 6H_2O$  (97%) and  $FeSO_4 \cdot 7H_2O$  (99% w/w) were acquired from Sigma-Aldrich. Acetonitrile, methyl, ethyl and propyl alcohols were acquired from Sigma-Aldrich (99% w/w) and were used as received. Limonene, (-)  $\beta$ -pinene and (-)  $\alpha$ -pinene were substrate selected (Sigma Aldrich, 99% w/w).

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### 2.2. Catalytic tests

Reactions under air were carried out in a glass reactor (50 mL) equipped with a magnetic stir bar and a septum. In a typical run, the catalyst was dissolved in CH<sub>3</sub>OH (ca. 25 mL), the reactor temperature was adjusted to 55 °C, and then substrate (12.5 mmol) was added and the reaction started. All nitrate salts and the iron salts were used in hydrated form as commercially available. When necessary, the system was first evacuated and submitted to gas flux (i.e., dioxygen) at room temperature and then pressurized to 0.10 MPa. Careful optimization of the stirring rate excluded the possibility of controlling by diffusion.

### 2.3. Reaction monitoring and product identification

Reactions were monitored by analyzing aliquots taken at regular time intervals by gas chromatography (Varian 450 instrument, FID, Carbowax 20 M capillary column). Conversions were estimated from the corresponding peak areas in comparison with the corresponding calibrating curves.

In general, the products were identified on a Shimadzu MS-QP 5050A mass spectrometer instrument operating at 70 eV, coupled with a Shimadzu 17A GC, by comparing the corresponding retention times with those of authentic samples and by inspecting the mass spectra. The procedures to purification by silica column as well as the data of NMR and FT-IR spectroscopy analyses of two main products are in the supplementary material.

### 3. Results and discussion

### 3.1. General aspects

Fe(NO<sub>3</sub>)<sub>3</sub> has been used as the reoxidant in the oxidation reactions of monoterpenes by dioxygen using palladium catalysts [10]. Generally, CH<sub>3</sub>COOH was used as solvent because the Pd(0) oxidation into Pd(II) occurs more quickly in protic solvent. However, oxidation selectivity is generally compromised by the solvent's acidity, which provokes concurrent reactions, such as carbon skeletal rearrangement followed by nucleophilic addition, lowering the yield of oxidation products [9,10]. For these reasons, the first objective herein was investigating the effect of CH<sub>3</sub>COOH replacement by CH<sub>3</sub>OH, in Pd(OAc)<sub>2</sub>/Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed monoterpene oxidation by dioxygen.

3.2.  $\beta$ -Pinene oxidation by dioxygen in Pd(OAc)<sub>2</sub>/M(NO<sub>3</sub>)<sub>n</sub>/CH<sub>3</sub>OH (M = Li (I), Cu(II) or Fe(III); n = 1, 2 or 3) system: Fe(III) cations as the real catalysts

As a general tendency, it can be observed that either conversion, as well as the selectivity obtained from the oxidation of  $\beta$ -pinene



Scheme 1. Main oxidation products of  $\beta$ -pinene by dioxygen in CH<sub>3</sub>OH solutions containing Fe(NO<sub>3</sub>)<sub>3</sub> in the presence or absence of palladium.

with dioxygen in the presence or absence of  $Pd(OAc)_2$ , were rigorously the same.

Although of Pd(OAc)<sub>2</sub> catalyst has remained stable throughout reactions (i.e., no Pd(0) formation was detected) (Exps. 1–3, Table 1), it was inactive in the  $\beta$ -pinene oxidation. Actually, the highest conversion and oxidation selectivity were reached in the only in the reactions where Fe(NO<sub>3</sub>)<sub>3</sub> was present, regardless of palladium presence. Thus, it can be concluded that Pd(OAc)<sub>2</sub> was an inactive catalyst in the  $\beta$ -pinene oxidation by dioxygen in CH<sub>3</sub>OH. Moreover, regardless of the cooxidants concentration, only Fe(NO<sub>3</sub>)<sub>3</sub> was an effective catalyst.

The major product of  $\beta$ -pinene oxidation was isolated and identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as myrtenol methyl ether (**1a**), a product previously obtained by us via Pd(II)-catalyzed oxidations (Scheme 1) [15].

Remarkably, among the nitrate salts employed, only Fe(NO<sub>3</sub>)<sub>3</sub> promoted the oxidation of  $\beta$ -pinene by dioxygen. It should be noted that the possibility of stoichiometric oxidation of  $\beta$ -pinene by NO<sub>3</sub><sup>-</sup> anions is discarded because both LiNO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> failed in the same reaction, even when used in stoichiometric proportions (i.e., considering the total reduction of NO<sub>3</sub><sup>-</sup> ions, entries 5 and 7, Table 1). Thus, it can be concluded that Fe(NO<sub>3</sub>)<sub>3</sub> salt truly acted as a catalyst in  $\beta$ -pinene oxidation by dioxygen.

Beyond promoting  $\beta$ -pinene oxidation by dioxygen, Fe(NO<sub>3</sub>)<sub>3</sub> catalyst also provoked its isomerization into two other monoterpenes and the conversion them into respective ethers (i.e., identified by GC-MS analyses) (Scheme 2).

### 3.3. Effect of $Fe(NO_3)_3$ catalyst concentration on the oxidation of $\beta$ -pinene

The discovery of Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed  $\beta$ -pinene oxidation by dioxygen was extremely welcome because the Pd(OAc)<sub>2</sub> is much more expensive than Fe(NO<sub>3</sub>)<sub>3</sub>. The Fe(NO<sub>3</sub>)<sub>3</sub> concentration effects on the conversion and selectivity of  $\beta$ -pinene oxidation were assessed in a broad range of concentrations (i.e., 0.010–1.200 mmol). The main results are summarized in the Table 2.

Table 1

$\beta$ -pinene oxidation by dioxygen in Pd(OAc) <sub>2</sub> /M(NO <sub>3</sub> ) <sub>n</sub> (M = Li(I), Cu(II) or Fe	e(III); n = 1, 2, or 3) system. <sup>a</sup>
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Exp.	Nitrate	Concentration (mmol)	Conversion (%)	Products selectivity (%)				
				Isomers <sup>b</sup>	Ethers <sup>⊂</sup>	Myrtenol methyl ether	Others <sup>d</sup>	
1 <sup>e</sup>	LiNO3	3.6	<3				100	
2 <sup>e</sup>	$Cu(NO_3)_2$	1.8	<3				100	
3 <sup>e</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>	1.2	97	12	20	62	6	
4	LiNO <sub>3</sub>	3.6	<3				100	
5		6.25	<3				100	
6	$Cu(NO_3)_2$	1.8	<3				100	
7		3.125	3				100	
8	Fe(NO <sub>3</sub> ) <sub>3</sub>	1.2	97	13	20	62	5	

<sup>a</sup> Reaction conditions: β-pinene (12.5 mmol); methyl alcohol (25 mL); 55 °C; dioxygen (0.10 MPa); 8 hour reaction.

<sup>b</sup>  $\alpha$  and  $\gamma$ -terpinenes were formed in almost equimolar amounts.

 $^{c}~\alpha$  and  $\gamma\text{-terpinyl}$  methyl ethers were formed in almost equimolar amounts.

<sup>d</sup> Complex mixture of non-identified minority products.

<sup>e</sup> Reaction containing Pd(OAc)<sub>2</sub> (0.010 mmol); no Pd(0) species were formed.



**Scheme 2.** Isomerization and oxidation products obtained in the Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed  $\beta$ -pinene oxidation reactions by dioxygen.

Actually, a novel oxidation process based on the use of  $Fe(NO_3)_3$  in catalytic amounts was developed (Table 2). The  $Fe(NO_3)_3$  catalyst was noticeably active; the highest TON and TOF were achieved (ca. 476 and 162 h<sup>-1</sup>, respectively; entry 1, Table 2). The results suggest that this catalyst is more effective than other transition metal salt catalysts described in literature [16]. The TOF displayed in the Table 2 was calculated to take into account the conversion reached within the first hour reaction; this is because, after this period, the decrease of substrate concentration affects the reaction rate.

Kinetic curves shown in the Fig. 1 reveal that a lowering on catalyst concentration resulted in a reduction of reaction rate, which reduced the final conversion in the reaction period studied herein. However, high TON values were achieved if compared to the other metal-catalyzed aerobic oxidation reactions [15].

# 3.4. Effect of gas phase and the source of Fe(III) ions on the oxidation of $\beta$ -pinene

The effect of gas phase was assessed using catalytic amounts of  $Fe(NO_3)_3$  or  $Fe(SO_4)_3$  under both inert or oxidant atmosphere (Table 3).

The changes of the gas phase does not impact either conversion or selectivity of reactions catalyzed by Fe(III) cations. The same effect was observed in changing the source of Fe(III) ions: Fe(NO<sub>3</sub>)<sub>3</sub> as well as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> were equally active and selective on  $\beta$ -pinene oxidation under air or dioxygen (Table 3).

The catalytic activity of  $Fe_2(SO_4)_3$  reinforces the observation made previously that Fe(III) cations are effective catalysts in the  $\beta$ -pinene

# **Table 2** Effect of Fe(NO<sub>3</sub>)<sub>3</sub> concentration on the conversion and selectivity of $\beta$ -pinene oxidation by dioxygen.<sup>a</sup>

Exp.	Fe(NO <sub>3</sub> ) <sub>3</sub> Conv. (%)		Selectivity (%)					
	(mmol)		Isomers <sup>b</sup>	omers <sup>b</sup> Myrtenol methyl ether		Oth <sup>d</sup>	TON <sup>e</sup>	${{{\rm TOF}^{\rm f}}\atop{(h^{-1})}}$
1	0.010	48	12	59	22	7	476	162
2	0.020	66	11	58	22	9	330	105
3	0.030	70	9	59	22	10	236	60
3	0.085	77	9	63	17	11	91	68
4	0.120	89	8	69	15	8	78	52
5	0.250	91	8	70	15	7	39	30
6	0.500	93	12	61	19	8	19	16
7	0.850	99	13	61	21	5	12	11
8	1.200	97	13	62	20	5	8	8

<sup>a</sup> Reaction conditions:  $\beta$ -pinene (12.5 mmol); methyl alcohol (25 mL); 55 °C; dioxygen (0.10 MPa); 8 hour reaction.

<sup>b</sup>  $\alpha$  and  $\gamma$ -terpinenes were formed in almost equimolar amounts.

 $^{c}~\alpha$  and  $\gamma\text{-terpinyl}$  methyl ethers were formed in almost equimolar amounts.

<sup>d</sup> Complex mixture of non-identified minority products.

 $^e$  Calculated in relation to Fe(III) cations: TON = [(% myrtenol methyl ether + % epoxides) / 100  $\times$  % conv/100]  $\times$  12.5/n mmol Fe(III) catalyst.

 $^{\rm f}$  Calculated in relation to the conversion obtained after 1 hour reaction (see Fig. 2): TOF = [(% myrtenol methyl ether + % epoxides)/100 × % conv (1 h)/100] × 12.5/n mmol Fe(III) catalyst.

oxidation by dioxygen. In addition, another auspicious result is that the catalytic activity of Fe(III) cations was not affected when air was the oxidant. Thus, this oxidative process is even more attractive from an economic and environmental viewpoint.

### 3.5. Effect of iron catalyst nature on the oxidation of $\beta$ -pinene

In Fig. 2, the kinetic curves obtained in the presence of different iron catalysts are shown. It is important to note that all of reactions were performed with the same iron concentration (0.50 mmol).

The results obtained reveals that the oxidation state of iron catalyst is a key aspect in the iron-catalyzed  $\beta$ -pinene oxidation reactions by dioxygen. Remarkably, Fe(III) salts were much more efficient catalysts than Fe(II) one. It was observed that FeCl<sub>3</sub> and mainly Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> were the more active catalysts, while the FeSO<sub>4</sub> was the least effective. Only a poor conversion (ca. 8%) after a 6-hour reaction was achieved in presence of Fe(II) catalyst.

### 3.6. Effect of temperature on the Fe(III)-catalyzed oxidation of $\beta$ -pinene

The reactions were performed using a low concentration catalyst (ca. 0.020 mmol), with the aim of making the effect of temperature more visible (Table 4).

Notably, under the lowest temperature (ca. 25 °C), the lowest conversion was reached (ca. 8%); in addition, reaction selectivity shifted in favor of the isomer formation (ca. 51% selectivity), with a consequent reduction in the selectivity obtained for ether (**1a**) (ca. 14%). Conversely, for temperatures equal to or higher than 35 °C, a sharp increase in the reaction conversions has been observed; oxidation selectivity was again favored and similarly to what was described in previous sections, ether (**1a**) was again the major product with selectivity in the range of 60%.



Fig. 1. Effects of Fe(NO<sub>3</sub>)<sub>3</sub> catalyst concentration on the  $\beta$ -pinene oxidation reactions by dioxygen.

#### Table 3

Effect of gas phase on the conversion and selectivity of the Fe(III)-catalyzed  $\beta\text{-pinene}$  oxidation reactions.ª

Exp.	Gas phase	Catalyst	Conv. (%)	Products selectivity (%)			
				Isomers <sup>b</sup>	Myrtenol methyl ether	Ethers <sup>c</sup>	Others <sup>d</sup>
1	02	Fe(NO <sub>3</sub> ) <sub>3</sub>	93	12 <sup>e</sup>	61	19	8
2	Air	$Fe(NO_3)_3$	93	11	58	19	12
3	02	$Fe_2(SO_4)_3$	93	10	62	18	10
4	Air	$Fe_2(SO_4)_3$	92	10	60	19	11

 $^{a}$  Reaction conditions:  $\beta\mbox{-pinene}$  (7.5 mmol); methyl alcohol (25 mL); Fe(III) catalyst (0.5 mmol); 8 hour reaction.

<sup>b</sup>  $\alpha$  and  $\gamma$ -terpinenes were formed in almost equimolar amounts.

 $^{c}\,\,\alpha$  and  $\gamma\text{-terpinyl}$  methyl ethers were formed in almost equimolar amounts.

<sup>d</sup> Complex mixture of non-identified minority products.

<sup>e</sup> Calculated in relation to Fe(III) cations.

The kinetic curves (Fig. 3) show that the initial rate was affected by the variations in the reaction temperature. Notably, within the first hour, all of the reactions occurred at the highest rates, regardless of the temperature employed. Nevertheless, after this period, a remarkable decrease was observed. Although the increasing of conversions continued, it occurred at a slower rate than the initial reaction period.

### 3.7. Effect of solvent

Aiming to improve the oxidation selectivity, reactions using different solvents were performed and the results are summarized in Table 5.



Fig. 2. Effect of iron catalyst nature on the  $\beta$ -pinene oxidation reactions by dioxygen.

### Table 4

Effect of temperature on the conversion and selectivity of  $\beta\mbox{-pinene}$  oxidation by dioxygen.^

Exp.	Temperature (°C)	Conv. (%)	Products se	TONd			
			Epoxides <sup>b</sup>	Myrtenol methyl ether	Ethers	Others <sup>c</sup>	
1	25	8	23	14	51	12	19
2	35	24	23	58	9	10	122
3	45	34	23	59	9	11	174
4	55	66	22	58	11	9	288

<sup>a</sup> Reaction conditions: β-pinene (12.5 mmol);  $Fe(NO_3)_3$  (0.020 mmol); methyl alcohol (25 mL); dioxygen (0.10 MPa); 8 hour reaction.

<sup>b</sup>  $\alpha$  and  $\gamma$ -terpinenes were formed in almost equimolar amounts.

<sup>c</sup>  $\alpha$  and  $\gamma$ -terpinyl methyl ethers were formed in almost equimolar amounts.

<sup>d</sup> Complex mixture of non-identified minority products.



**Fig. 3.** Effect of temperature on  $Fe(NO_3)_3$ -catalyzed  $\beta$ -pinene oxidation reaction rate by dioxygen.<sup>a</sup>. <sup>a</sup>Reaction conditions:  $\beta$ -pinene (12.5 mmol);  $Fe(NO_3)_3$  (0.020 mmol); methyl alcohol (25 mL); dioxygen (0.10 MPa); 8 hour reaction.

The formation of methyl ether (1a) is linked to the use of methyl alcohol. For this reason, when using another solvent, the formation of this product was not observed. However, similar to that observed using methyl alcohol as solvent, the main product obtained in the reaction with ethyl alcohol was also an ether, namely myrtenol ethyl ether, which was obtained with modest selectivity (46%). The catalyst was completely insoluble in propyl alcohol and consequently the reaction was not performed. In CH<sub>3</sub>CN, the catalyst was partially soluble; the solution became slightly yellow, however, there still remained a part of solid catalyst. At the end of the reaction, although no ether was obtained,  $\alpha$ -terpineol (15%) was the major product (see footnote Table 5).

The catalyst was completely insoluble in propyl alcohol and consequently the reaction was not performed. In  $CH_3CN$ , the catalyst was partially soluble (i.e. the colorless pale yellow was observed and a solid remained in the reaction). At reaction end, although no ether has been obtained, myrtenic acid (15%) was the major product (see footnote Table 5).

3.8. Insights into a possible mechanism of Fe(III)-catalyzed oxidation  $\beta$ -pinene by dioxygen in CH<sub>3</sub>OH

Iron catalysts containing nitrogen ligands are frequently used for dioxygen activation in the oxidation reactions [13]. Different mechanisms have been proposed in which is postulated that these reactions

Table 5

Effect of solvent on the conversion and selectivity of the Fe(NO\_3)\_3-catalyzed  $\beta\text{-pinene}$  oxidation reactions.^a

]	Exp.	Solvent	Conv. (%)	Products selectivity (%)				
				Isomers <sup>b</sup>	Oxidation Products	Myrtenol alkyl ethers	Ethers <sup>d</sup>	Others <sup>e</sup>
	1	CH₃OH	93	12	-	61	19	8
2	2	$C_2H_5OH$	70	28	-	46	21	5
	3 <sup>f</sup>	C <sub>3</sub> H <sub>7</sub> OH	-	-	-	-	-	-
4	4 <sup>g</sup>	CH <sub>3</sub> CN	25	46	29 <sup>c</sup>	-	-	25

<sup>a</sup> Reaction conditions:  $\beta$ -pinene (7.5 mmol); solvent (25 mL); Fe(III) catalyst (0.5 mmol); 8 hour reaction.

<sup>b</sup> α and γ-terpinenes were formed in almost equimolar amounts.

<sup>c</sup> The oxidation products were formed with the selectivity as follow: pinocarveol (9%);  $\alpha$ -terpineol (15%); myrtenic acid (5%).

 $^{
m d}$   $\alpha$  and  $\gamma$ -terpinyl methyl ethers were formed in almost equimolar amounts.

<sup>e</sup> Complex mixture of non-identified minority products.

<sup>f</sup> The reaction in C<sub>3</sub>H<sub>7</sub>OH was not performed because the catalyst was totally insoluble.

<sup>g</sup> The Fe(NO<sub>3</sub>)<sub>3</sub> catalyst was partially soluble in CH<sub>3</sub>CN.



Scheme 3. Proposed mechanism for Fe(III)-catalyzed oxidation of  $\beta$ -pinene to myrtenol methyl ether by dioxygen.

involve the formation of iron-hydroperoxo adduct between the catalyst and olefin [13,17]. In addition, it should be highlighted that the large number of products obtained supports the hypothesis that autoxidation also takes place in those reactions.

In general, mechanisms involving intermediate species containing iron cations with high oxidation numbers (i.e., Fe(V) = O) have been reported [13,16–18]. However, different from the most of the results described in the literature, the Fe(III)-catalyzed oxidation reactions described herein occurred in the absence of nitrogen ligands; thus, we think that Fe(V) = O species are not sufficiently stable to be formed. Actually, a detailed mechanism of iron-catalyzed oxidation reactions described herein is not clear at the present stage. However, mechanisms based on stabilization of Fe(IV) oxo intermediate species in Fe(acac)<sub>2</sub>-catalyzed oxidation by dioxygen in alcohol medium reactions were recently described [19]. Thus, based on our experimental findings and on the literature, a mechanism could be proposed (Scheme 3).

Focusing on the formation of ether (1a) as the main oxidation product, it is concluded that the presence of methoxy group makes the participation of a solvent obligatory. We suggest that, in the presence of dioxygen and Fe(III) cations, the CH<sub>3</sub>OH is converted into highly active methoxyl species, which in the presence of Fe(IV)–OOH intermediates reacts with  $\beta$ -pinene, oxidizing it into ether (**1a**) and regenerating Fe(III) cations (Scheme 3). Similar to that described in the literature. we think that the presence of CH<sub>3</sub>OH stabilizes the Fe(IV) intermediate species [19-21].

It is important to highlight that the allylic radical formed initially from  $\beta$ -pinene oxidation (which was omitted in the Scheme 3 by simplification), may be isomerized into a more stable allylic radical with the carbon skeletal similar to the  $\alpha$ -pinene (i.e. where the unpaired electron occupies the exocyclic allylic position in relation to internal double bond) [2]. This proposal is supported by the fact that the same product (1a) was the major oxidation product obtained in the  $\alpha$ -pinene oxidation reactions (see supplementary material).

### 4. Conclusions

A nitrogen ligand-free protocol was developed for Fe(III)-catalyzed oxidation of monoterpenes by dioxygen in methyl alcohol. Simple iron salts (i.e., Fe(NO<sub>3</sub>)<sub>3</sub> or Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> hydrate) were highly efficient catalysts in promoting selective oxidation by dioxygen of  $\beta$ -pinene and  $\alpha$ -pinene (see Supplementary material) into myrtenol methyl ether or epoxide derivatives in CH<sub>3</sub>OH. Notably, the catalytic oxidation of these monoterpenes was performed in the absence of palladium. High TONs. TOFs. and selectivity were obtained in oxidation reactions, and assessed at different conditions. This protocol is a straightforward synthesis method of monoterpene ethers in a nitrogen ligand-free system, which uses molecular oxygen as a stoichiometric oxidant, and cheap and commercially available iron salts as catalysts.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2013.08.018.

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