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Synthesis of peroxophosphotungstate immobilized onto polymeric support as heterogeneous catalyst for the epoxidation of unsaturated fatty esters

Evelyne Poli, Jean-Marc Clacens, Yannick Pouilloux*

Université de Poitiers, Laboratoire de Catalyse en Chimie Organique, CNRS, UMR 6503 ESIP, 40, avenue du Recteur Pineau, 86022 Poitiers Cedex, France

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ABSTRACT

Phosphotungstate-based catalysts are efficient catalyst for epoxidation of unsaturated fatty methyl esters but the separation and the reuse of the catalyst are extremely difficult. For that reason, we have prepared different polyoxotungstate catalyst supported onto amphiphilic resins by anionic exchange. We have tried to control the resin amphiphilic characters by varying the imidazole group nature, as well as the spacer linker on the support. This heterogeneous catalyst exhibits excellent activity in the epoxidation of methyl-9,10-octadecenoate with aqueous H2O2 and can be easily recycled without loss of performance.

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1. Introduction

Renewable raw materials are environmental friendly, biodegradable, low cost and readily available. Vegetable oils rich in polyunsaturated chain may be used to introduce functional groups such as epoxide. The epoxidation of carbon–carbon double bond is one among many transformations and applications which deserve particular attention. In fact, epoxides and particularly epoxidized fatty acids are by-products that are already largely used in industrial processes such as polyvinyl chloride (PVC) thermal stabilizer [1–3]. Indeed, methyl octadecenoate epoxide is an intermediate of the polymers chemistry (such as the class of polyurethanes, polycyanates), in the lubricants and detergents synthesis, and in the formulation of biofuels [4]. They are also important intermediates in organic synthesis in the formation of diols, polyols, polyethers, amino-alcohols, etc. [5]. Many technologies are used to produce epoxides (percarboxylic acids, peroxides, oxygen, enzymes). Industrially the epoxidation of fatty esters uses a mixture of formic acid/hydrogen peroxide or peracids [6]. This process induces the formation of various by-products, and the solvents elimination is needed. The direct epoxidation of unsaturated fatty compounds by H_2O_2 as oxidant was investigated since H_2O_2 is a good candidate to develop a green process. It is cheap, readily available and transformed into water as the only by-product. Moreover, that is easy to eliminate by decantation because of the biphasic system. During the last decade, many different catalytic systems for the epoxidation using hydrogen peroxide have been studied [7–9].

Tungsten-based catalysts including polyoxometalates (POM) usually show high epoxide selectivity [10–12]. Previously, we have obtained a high epoxide yields in a presence of a peroxophosphotungstate catalyst and hydrogen peroxide by working under air or oxygen flow [13]. But the main problem is the separation and reuse of the catalyst. For that reason, we have tried to immobilize the polyoxotungstate anion onto supports. The homogeneous active species may be linked in various ways to its support: by ionic interactions (ionic bonds, van der Waal), or by covalent bonds, the support could be organic as resin or inorganic as silica depending on the reactant properties. Recently, the development of easily recoverable and recyclable solid catalysts based on POMs supported on silica were described by Mizuno et al. [14–19]. They described ruthenium catalysts supported on alumina and titania which have better catalytic properties on olefin and alcohol epoxidation. It also possible to support the POM species onto polymeric resin [20,21]. The anion $\{PO_4\ [WO(O_2)_2]_4\}^{3-}$ supported on a resin Amberlite IRA-900 ion exchange system provides a heterogeneous epoxidation with high yields using only 2 equivalents of H_2O_2 30% in acetonitrile at 311 K [18]. Another method is the immobilization of peroxophosphotungsten complex on modified polymers with organophosphorous ligands [22]. To control of the hydrophobicity of the silica surface, Neumann et al. have supported $(\{PO_4[W(O)_2(O_2)]_4\}^{3-})$ on silica particles modified by substitution of OH groups by phenyl groups [23]. To facilitate interaction with the catalytic center, the POM anion is stabilized via a quaternary

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* Corresponding author. Tel.: +33 0 5 49 45 3; fax: +33 0 5 49 45 3.
E-mail address: yannick.pouilloux@univ-poitiers.fr (Y. Pouilloux).

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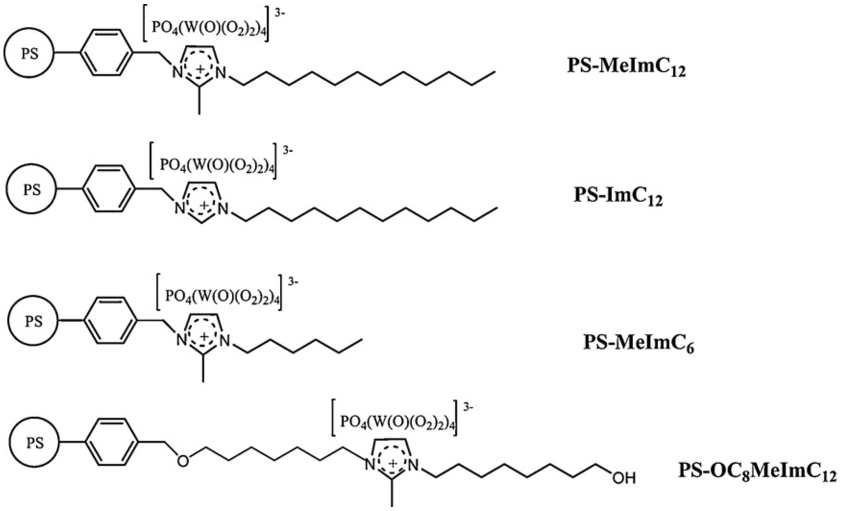

Fig. 1. Structure and name of the synthesized resins.

ammonium cation located on alkyl carbon chain grafted on silica surface. This system catalyzes the epoxidation of alkenes using 30% H_2O_2 as oxidant in free solvent. Mizuno et al. [24] have also developed a complex structure where the POM is supported by ionic interaction to a support resin/ionic liquid, the ionic liquid is supported covalently to a silica support. This catalytic system allows many alkenes epoxidation in the presence of H_2O_2 30% and nitriles as solvent with yields comprised between 80 and 100%. To prepare this catalyst, the ionic liquid part is synthesized, and then covalently grafted to the silica support. Finally, by ion exchange on the quaternary ammonium ionic liquid part, the peroxophosphotungstate is immobilized. With this technique, there is no problem of hydrophilicity of the silica surface, which prevents easy access to organic solvents, and no basic sites to decompose the oxidant.

We decided to prepare different peroxophosphotungstate catalyst supported onto amphiphilic resins by ion exchange to obtain an amphipilic catalyst.

2. Experimental

2.1. Synthesis of the catalysts

The structure and name of the synthesized catalysts are presented in Fig. 1.

2.1.1. PS-MeImC$_{12}$, PS-ImC$_{12}$, PS-MeImC$_6$ resins

In a typical procedure, the Merrifield resin (1.4–1.6 mmol Cl/g Acros, 2 g) and methylimidazole (Acros, 2 g) or imidazole were added under N_2 flow in the presence of Na_2CO_3 (Normapures for analyses, 0.653 g) and DMF (Fluka,10 mL) and the mixture was placed under stirring at 373–383 K and under inert atmosphere during 15 h in order to link the imidazole on resin. After washing by dichloromethane and water until the filtrate pH is neutral, the resin was placed under vaccum at 353 K during 12 h. This resin was then placed under inert atmosphere with bromododecane (5 mL) or bromohexane and stirred 72 h at 353 K under inert atmosphere. The resin was washed with dichoromethane, ethanol and acetone to dry it. Finally, the solid was placed with the aqueous phase of the peroxophosphotungstate catalyst prepared as described by Venturello [10]. After filtration and washing with distilled water, heptane and acetone, a light yellow resin was obtained.

2.1.2. PS-OC$_8$MeImC$_{12}$ resin

2-Methylimidazole (Acros, 2 g) and 8-chloro-1-octanol (Acros, 4 g) were placed with Na_2CO_3 (Normapures for analyses, 0.656 g) and DMF (Fluka, 10 mL) under inert atmosphere. The mixture was placed under stirring at 373–383 K and under inert atmosphere during 15 h. The resin was filtrated on fritted and washed by dichloromethane and then distilled water until the filtrate pH is neutral. Finally the resin was washed by acetone to dry it. The obtained resin was placed under vacuum and temperature (353 K) during 12 h. The solid obtained was placed with Merrifield resin (1.4–1.6 mmol Cl/g Acros, 1.5 g) and DMF (10 mL) under inert atmosphere, stirring 24 h at 373–383 K. The resin was washed on fritted with dichoromethane, ethanol and acetone. Finally, the solid was placed with the aqueous phase of the peroxophosphotungstate catalyst prepared as described by Venturello et al. [10] After filtration and washing with distilled water, heptane and acetone a light yellow solid was obtained.

2.2. Epoxidation procedure

In a double-walled reactor (with internal diameter of 16 mm) the peroxophosphotungstate supported catalyst was exactly weighted directly into the reactor (0.094 mmol), then the methyl oleate (MO) (99% Aldrich, 3.37 mmol) was added under strong stirring. When a temperature of 338 K was reached, H_2O_2 35% w/v (990 μL) were added in three times. At the end of the reaction, the mixture was first filtered on fritted. The resin catalyst was recovered on the fritted, washed with ethyl acetate and reused for other test. The organic phase was then recovered and extracted with 20 mL of ethyl acetate (99% Carlo-Erba) and dried on $MgSO_4$. After evaporation of the solvent, the products were analysed by GC and HPLC.

2.3. GC analysis

All the compounds were analysed using a Varian 3350 GC equipped with an FID detector and an On-column injector. An HT5 column (25 m × 0.32 mm × 0.1 μm) from SGE was used. The injector and detector temperatures were, respectively, of 323 K and 573 K. The carrier gas was nitrogen. For analyte separation, the GC oven temperature was fixed at 343 K for 1 min, then ramped at a rate of 10 K/min to 473 K, and ramped at 25 K/min to 573 K then kept constant for 1 min.

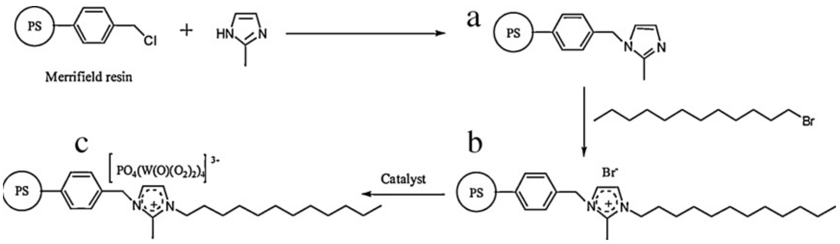

Fig. 2. Scheme of the peroxophosphotungstate resin preparation method.

To prepare the sample to be analysed in a pillbox, weight around 0.1 g of the obtained product, around 0.05 g of the external standard and 800 μL of solvent (ethyl acetate). After stirring the sample is injected into GC (0.1 μl).

The methyl oleate conversion is expressed as follows at *t* time:

$$\text{Conversion} \quad (\%) = \frac{S^i_{\text{oleate}}/S^i_{\text{dod}} - S^t_{\text{oleate}}/S^t_{\text{dod}}}{S^i_{\text{oleate}}/S^i_{\text{dod}}} \times 100$$

with S^i_{oleate}, surface of the methyl oleate chromatographic peak at time zero; S^i_{dod}, surface of the dodecane chromatographic peak at time zero; S^t_{oleate}, surface of the methyl oleate chromatographic peak at time *t*; S^t_{oleate}, surface of the dodecane chromatographic peak at time *t*.

The epoxide yield is expressed as follows at *t* time:

$$\text{Yield} \quad (\%) = \frac{S^t_{\text{epox}}/S^t_{\text{dod}} \times K_{\text{oleate}}}{S^i_{\text{oleate}}/S^i_{\text{dod}} \times K_{\text{epox}}} \times 100$$

with S^t_{epox}, surface of the epoxide chromatographic peak at time *t*; S^t_{dod}, surface of the dodecane chromatographic peak at time *t*; S^i_{oleate}, surface of the methyl oleate chromatographic peak at time zero; S^i_{dod}, surface of the dodecane chromatographic peak at time zero; K_{oleate}, relative response factor of the MO compared with dodecane; K_{epox}, relative response of the epoxide compared with dodecane.

The epoxide selectivity is expressed as follows:

$$\text{Selectivity} \quad (\%) = \frac{\text{Yield} \quad (\%)}{\text{Conservation} \quad (\%)} \times 100$$

The carbon balance is calculated from the initial mole of reactants from GC analysis. All the yields were determined thanks to calibrated GC peaks area.

2.4. LC analysis

All the compounds were analysed using a Waters HPLC 600 Controller equipped with a Waters UV 486 Tunable Absorbance Detector and a Waters 600 Pump. The column was a Nucleosil C_{18} (250 mm × 4.6 mm × 5 μm) from Supelco and an autosampler Waters 717 plus was used. The analyses were done at room temperature with a 205 nm wavelength, and the solvent was methanol (Aldrich HPLC grade) with a flow of 1 mL/min.

2.5. ICP analysis

The ICP analyses were performed with an ICP/ES Perkin-Elmer Optima 2000 DV.

The resin composition ratio P/W is expressed as follow:

The POM formula is $PW_4O_{24}{}^{3-}$ and the theoretical ration P/W is expressed as following:

$$\frac{P}{W_{\text{theo}}} = \frac{1}{4} = 0.25$$

$P/W_{\text{exp}} = \frac{\%P/M_P}{\%W/M_W}$ with %P and %W the weight percentage of phosphor and tungsten obtained by ICP.

2.6. FTIR analysis

The IR analyses were performed with a Sectrom one spectrometer (Perkin-Elmer) equipped with a DRIFT Saphire cell.

3. Results and discussion

The activity of the peroxophosphotungstate catalyst for the epoxidation of *cis* methyl octadecenoate with aqueous hydrogen peroxide at 338 K under O_2 flow and without solvent was investigated with a series of POM supported on polymer resin. As the reactants are not missibles, an amphiphilic catalytic system which plays a role of phase transfer agent was developed. The POM anion is immobilized by ionic exchange with a quaternary ammonium cation which is covalently grafted onto polystyrene resin (Fig. 2).

3.1. Resins functionalisation and characterization

We have chosen a polymeric Merrifield resin as support which has an aromatic cycle and an alkyl chain that gives lipophilic properties (Fig. 2A).

Owing to large size of the peroxophosphotungstate anion, the imidazolium group is a quaternary ammonium group appropriate to support it. Indeed, imidazole ring was generally proposed to prepare ionic liquid. Moreover, if both nitrogen atoms of the imidazole ring are substituted, there is a delocalization of total charge available on the entire aromatic ring, which increases its total positive charge improving the stabilization of peroxophosphotungstate anion. But due to the steric constraints of peroxophosphotungstate anion, the imidazole cannot be directly linked to the polystyrene support (Fig. 2A). Thus, a benzene ring has been inserted between the polystyrene support and imidazole group. Finally, as the reactant is the methyl oleate which has an alkyl chain of 18 carbons, a C12 alkyl chain is covalently grafted on the imidazole ring to increase the hydrophobic balance of catalyst (Fig. 2B). To assist the approach and the contact of the unsaturation of methyl ester with the anion peroxophosphotungstate, the C12 chain present on the support allows better positioning in space and favors the adsorption of the C18 chain of methyl ester. Then, to modify the hydrophilic/lipophilic balance of the resin, several changes were made. To increase the amphiphilic character, the imidazole was replaced by a methylimidazole ring to get the resin called PS-MeImC_{12}. To highlight the interest of the C12 alkyl chain, it has been replaced by a much shorter chain alkyl, C6 to get the resin called PS-MeIMC_6. Finally, to overcome a steric problem of peroxophosphotungstate anion which would hardly be supported by imidazole, a resin was performed with an additional spacer arm between the support and the methylimidazole ring (PS-$\text{OC}_8\text{MeImC}_{12}$). These different structures of resins are shown in Fig. 2.

Table 1
Chemical composition of the synthesized resins (weight %).

Resins	C%	H%	N%	P%	W%	P/W_{theo}	P/W_{exp}
PS-ImC_{12}	75.46	8.24	2.64	0.24	5.42	0.25	0.26
PS-$MeImC_{12}$	75.31	7.68	2.65	0.23	4.81	0.25	0.28
PS-$MeImC_6$	82.05	8.08	3.11	0.23	4.84	0.25	0.28
PS-OC_8MeImC_{12}	60.91	6.83	2.50	0.81	18.60	0.25	0.26

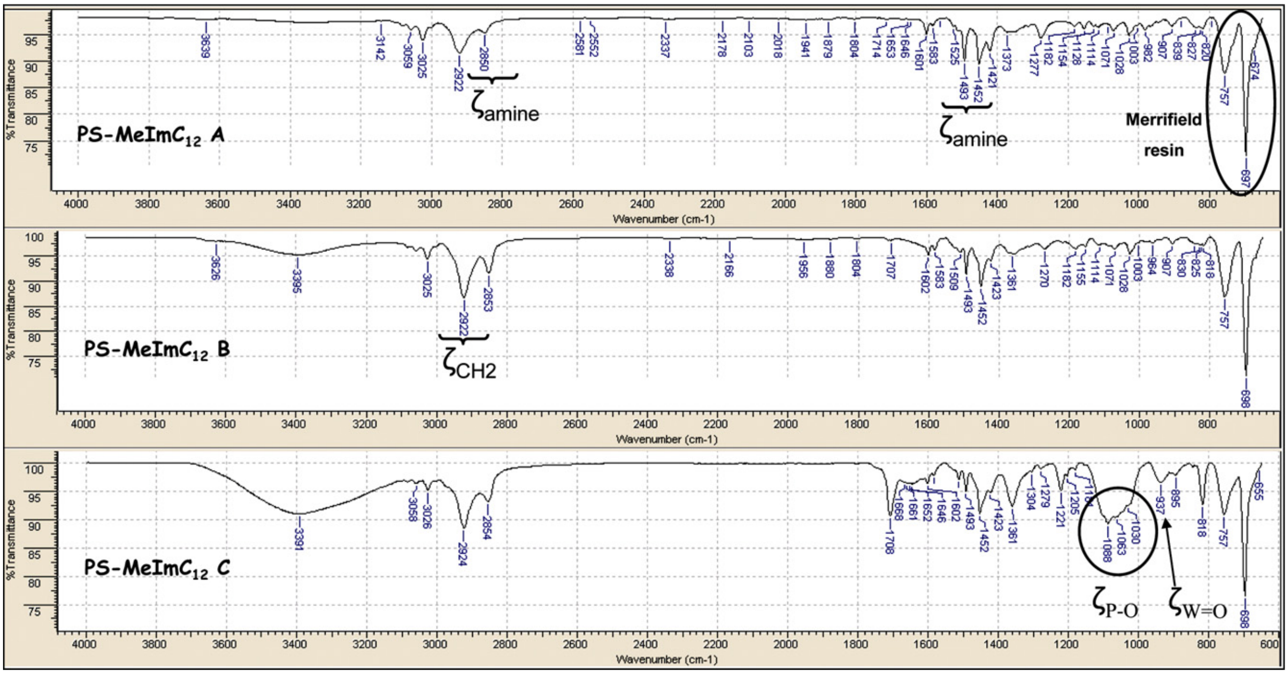

Fig. 3. IR analysis of the PS-$MeImC_{12}$ at different steps of the synthesis (A, B and C, as reported in Fig. 2).

All the synthesized resins were analysed by FTIR and ICP/ES analysis to control the presence of the POM species at different steps of the synthesis. As shown in Table 1, the chemical composition and the P/W ratios experimental (noted exp) and theoretical (theo) of the resins are similar. These results prove that the different steps of the catalyst synthesis do not change the structure of the synthesized anions.

The grafting level has been calculated and varies from 6 to 8% excepted in the case of the PS-OC_8MeImC_{12} solid where the grafting percentage is equal to 29%.

In all cases, the IR analysis showed the characteristics bands of the imidazole (1400–1500 cm^{-1}). Bands at 1088, 1058 and 1035 cm^{-1} are attributed to oxygen interaction with the phosphorous and the bands between 960 and 800 cm^{-1} are attributed to oxygen interaction with tungsten in accordance with the IR analyses described by Zapata et al. [25]. In Fig. 3, we showed the IR analysis of the PS-$MeImC_{12}$ at different steps of the synthesis and we can see that the structure is kept during the preparation.

3.2. *Cis methyl-9,10-octadecenoate epoxidation*

The different POM – resins were tested in the epoxidation reaction of *cis* methyl-9,10-octadecenoate. The reaction was performed with aqueous hydrogen peroxide (H_2O_2/MO ratio: 6/1 as oxidant at 338 K under O_2 flow (50 mL/min) and without solvent. The amphiphilic properties of the resins can play a role of phase transfer catalyst between the ester phase and the H_2O_2 aqueous phase and avoid the using of solvent. The catalytic efficiencies of the different synthesized catalysts are presented Table 2.

Table 2
Epoxidation of *cis* methyl octadecanoate with the different synthesized resins.[a]

Entry	Resins	Conversion[b] (%)	Epoxide yield[b] (%)	Epoxide selectivity[b] (%)	Alcohols selectivity[c] (%)	%P[d]	%W[d]
1	PS-ImC_{12}	54.1	9.2	17.0	83.0	0.24	5.42
2	PS-ImC_{12} recycled	54.8	6.2	10.7	89.3	0.23	5.38
3	PS-$MeImC_6$	62.5	12.6	20.1	71.6	0.23	4.84
4	PS-$MeImC_6$ recycled	58.6	11.6	19.8	80.1	0.22	4.82
5	PS-$MeImC_{12}$	50.0	30.0	60.0	3.0	0.23	4.81
6	PS-$MeImC_{12}$ recycled	46.1	28.3	61.4	3.0	0.13	4.50
7	PS-OC_8MeImC_{12}	92.6	14.3	15.4	84.2	0.81	18.60
8	PS-OC_8MeImC_{12} recycled	92.5	14.6	15.8	84.2	0.77	14.70

[a] Epoxidation conditions: 1 h, 338 K, H_2O_2/MO (6/1), O_2 50 mL/min.
[b] Determined by GC analysis.
[c] Determined by LC analysis. The alcohols determined by LC–MS are the methyl-9-hydroxy-octadecenoate and the methyl-9,10-dihydroxyoctadecenoate.
[d] Determined by ICP analysis.

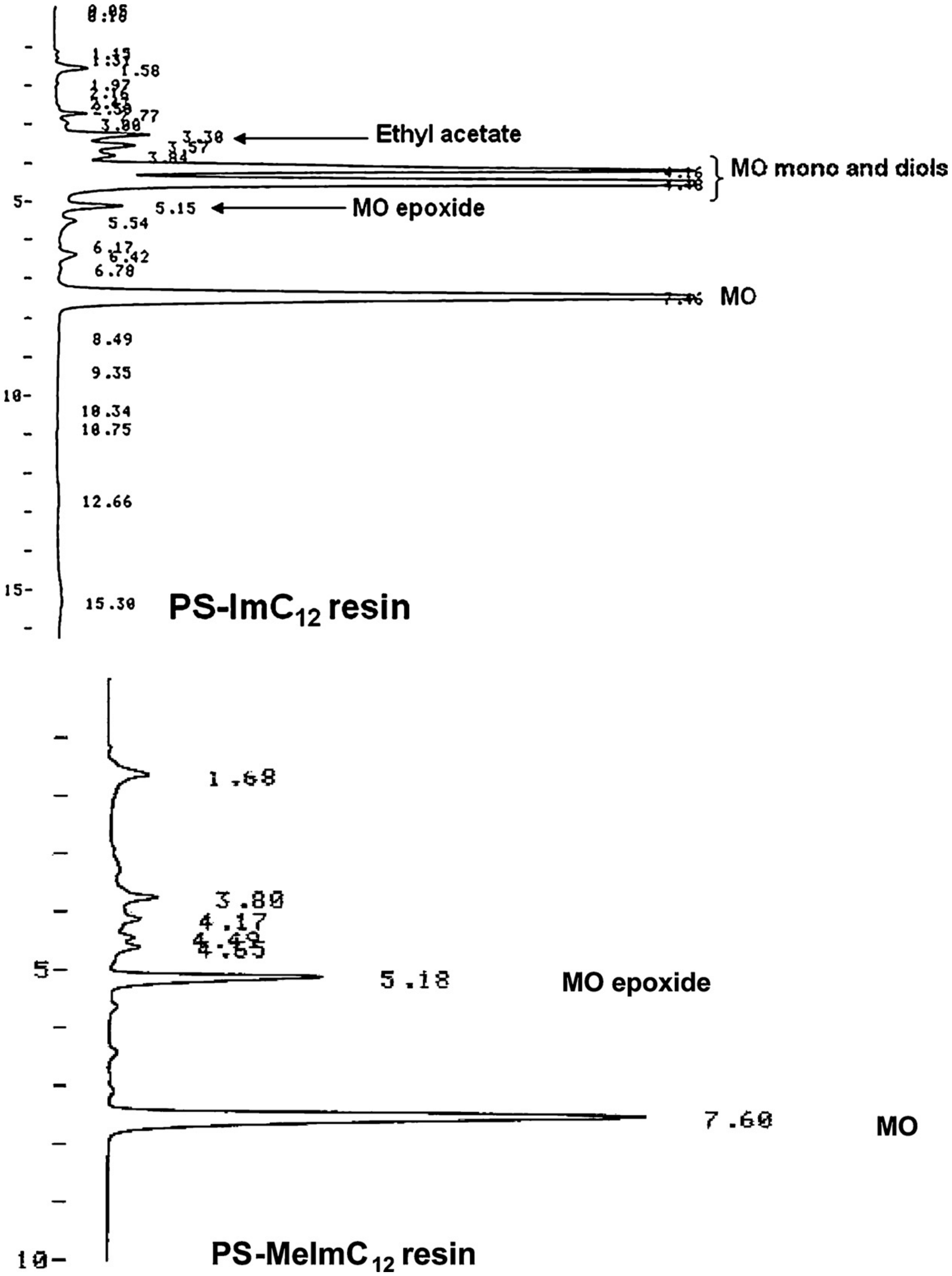

Fig. 4. LC analysis of mixture reaction in the presence of resins (a) PS-ImC$_{12}$ and (b) PS-MeImC$_{12}$.

Firstly the resin PS-ImC$_{12}$ (entry 1) was used to perform the epoxidation reaction under O_2 flow. The *cis* methyl-9,10-octadecenoate (MO) conversion is 54.1% but the epoxide yield and selectivity are very low (9.2 and 17%, respectively). The LC (Fig. 4) and LC–MS (Fig. 5) analysis showed that the main products of the reaction are fatty alcohols (methyl-9-hydroxy-octadecenoate and methyl-9,10-dihydroxyoctadecenoate) since the alcohols selectivity is equal to 83%, a similar result is described previously [26] at the beginning of the reaction when the reaction is performed in the presence of homogeneous POW catalyst. The results show that

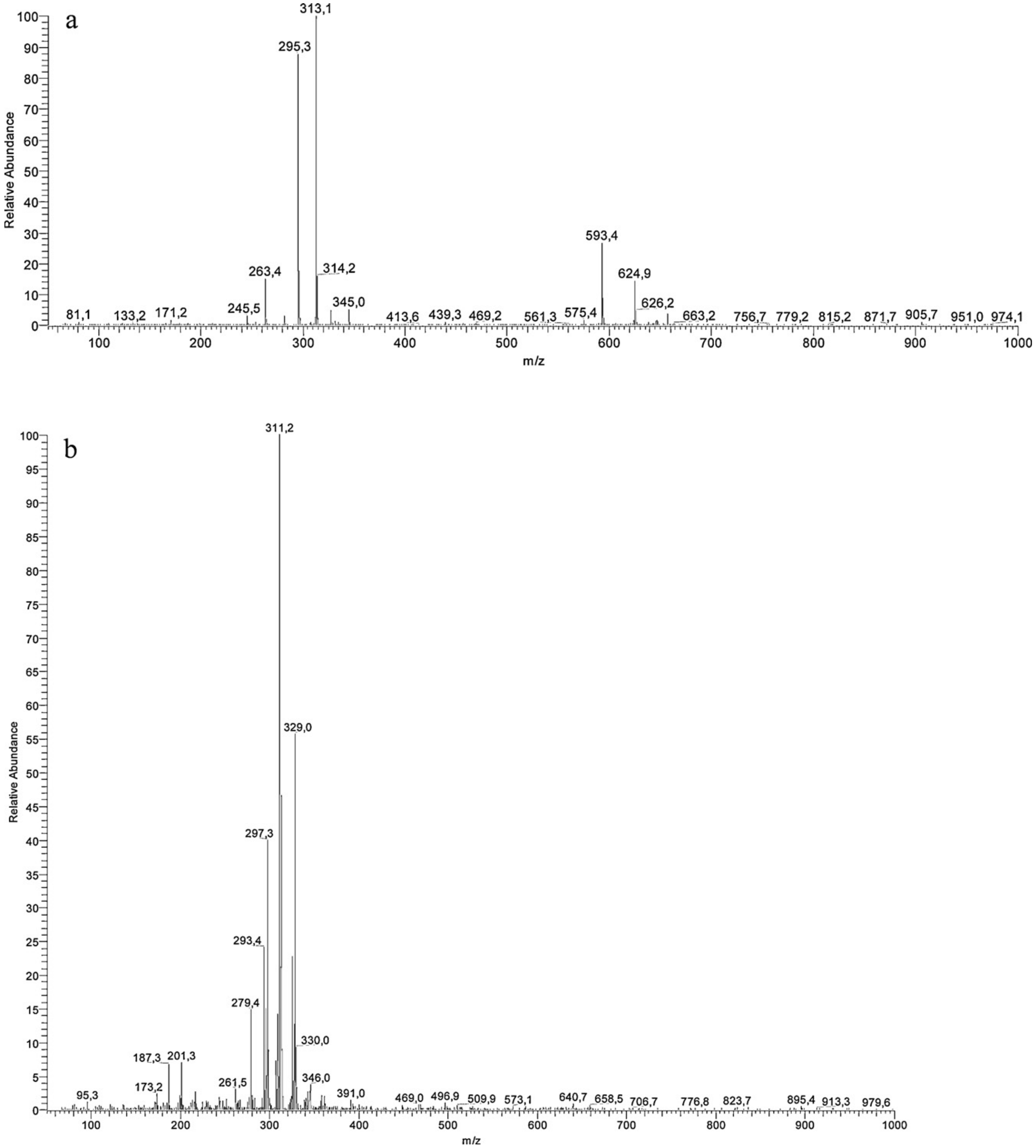

Fig. 5. LC–MS analysis of the (a) methyl-9-hydroxy-octadecenoate and (b) methyl-9,10-dihydroxyoctadecenoate.

this resin PS-ImC$_{12}$ which is very lipophilic favours the fatty alcohols formation instead of the epoxide formation. The catalyst has a great affinity to the ester phase and the epoxidation with H_2O_2 is limited. In these conditions, the O_2 flow favors the oxidation of double bond to alcohol (mono- and diol).

The resin was recovered by filtration, washed with ethyl acetate and dried. Then, the resin has been reused without significant loss activity (entry 2). The ICP analysis of the resin PS-ImC$_{12}$ after each cycle confirms that the catalyst is stable.

To underlined the importance of the fatty alkyl chain of the resin PS-ImC$_{12}$ the resin PS-MeImC$_6$ was synthesized and used in the epoxidation reaction (entry 3). The methyl-9,10-octadecenoate conversion increases from 54% to 62.5% which indicates that the hydrophilic/lipophilic balance is improved. Indeed the epoxide yield and selectivity increase, respectively, to 12.6 and 20.1% but the main compounds after 1 h of reaction are alcohols. It seems that the reduction of the size of alkyl chain on imidazole favours the contact between methyl octadecenoate and oxidant agent and consequently the conversion and selectivity to epoxide. Moreover, the presence of methyl group on nitrogen also modifies the catalytic properties by improvement of the imidazolium cation charge.

The catalyst can be reuse without lost of activity (entry 4). Additionally the ICP analysis of the catalyst shows that no modification of catalyst composition is observed after the reaction or its recycling.

A solution to increase the epoxide yield could be to slightly increase the lipophilic properties of the PS-ImC_{12} resin by introducing a methyl to the imidazole group to form the resin noted PS-MeImC_{12} (entry 5). This resin seems to be a promising catalyst since the MO conversion is still 50% but the epoxide yield and selectivity strongly increase, respectively, to 30% and 60%. The alcohols formation generally observed with previous resins is strongly limited, only 3%. With this resin PS-MeImC_{12} the epoxide product is the most important as showed on Fig. 3a and b which compared the results obtained in the presence of PS-ImC_{12} and PS-MeImC_{12} after 1 h of reaction time. One can see that the mono- and diols compounds are mainly formed over PS-ImC_{12} whereas the main product is the methyl epoxyoctadecane over PS-MeImC_{12}. This catalyst presents the best hydrophilic/lipophilic balance leading to the higher epoxide selectivity.

The resin was recycled and reused in a new experiment (entry 6). It gives the same results. Moreover the ICP analysis showed the POM structure of the resin was conserved after reuse.

Then, we have increased the reaction time successively 2 h, 24 h and 48 h. No significant increasing in epoxide selectivity was observed. Then, the reaction was carried out at higher temperature and higher oxidant content without changing the selectivity to epoxide–octadecane. To control that the POM catalyst is not released in the medium, the reaction has been performed in the presence of the catalyst for 15 min, then it was removed from the middle and the reaction was continued. No increase of methyl-9,10-octadecenoate conversion and epoxide selectivity was observed.

Due to the size of the peroxophosphotungstate complex, we tried to improve the contact between the methyl-9,10-octadecenoate and the active site by increasing the distance between support and the imidazolium cation. A spacer arm (–OC_8) was then added between the polymeric support and the imidazole group which support the peroxophosphotungstate anion (PS-OC_8MeImC_{12}). It also contains an ether bond which increases the amphiphilic balance.

As expected, in the presence of the resin PS-OC_8MeImC_{12} (entry 7), the methyl-9,10-octadecenoate conversion is very high (92.6%) due to more POM species on the support, but the epoxide yield and selectivity are low (14.3 and 15.4%, respectively), the alcohols formation is more significant (84.2%). We also observed the formation of cleavage compounds such as nonanal or nonanoïc acid.

The addition of the spacer arm –OC_8 to the structure of the resin for increasing its amphiphilic property and optimize the approach of the methyl-9,10-octadecenoate, seems preferentially favor the oxidation of the MO unsaturation to form preferentially its alcohols and cleavage compounds. This is due to the acidity of the catalyst which is higher since the grafting level is more important on PS-OC_8MeImC_{12}.

4. Conclusion

The epoxidation of methyl-9,10-octadecenoate with H_2O_2 under O_2 flow in the presence of polyoxometalate supported on polymer resin was studied. To do that, different peroxophosphotungstate anions were stabilized by ionic exchange with imidazolium cation covalently grafted onto resin. We have showed that the catalytic properties vary with the hydrophilic/lipophilic balance (carbon chain number, spacer arm between benzene cycle and imidazole group, N-substitution of imidazole ring). The best result in epoxidation is obtained in the presence of the PS-MeImC_{12} catalyst which has a C12 carbon chain, a N-methyl substitution of imidazole. The conversion is equal to 50% and the selectivity to epoxide close to 60%. Moreover, it also is recycling showing a good stability of POM species on the catalyst.

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