



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

ARTICLE INFO

Article history:

Received 29 June 2010

Received in revised form 2 November 2010

Accepted 3 November 2010

Available online 8 December 2010

Keywords:

Epoxidation

Methyl oleate

Polyoxotungstate

Immobilization

H₂O₂

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.

Published by Elsevier B.V.

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 H₂O₂ as oxidant was investigated since H₂O₂ 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 {PO₄[WO(O)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 H₂O₂ 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 ({PO₄[W(O)₂(O₂)]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

* 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).

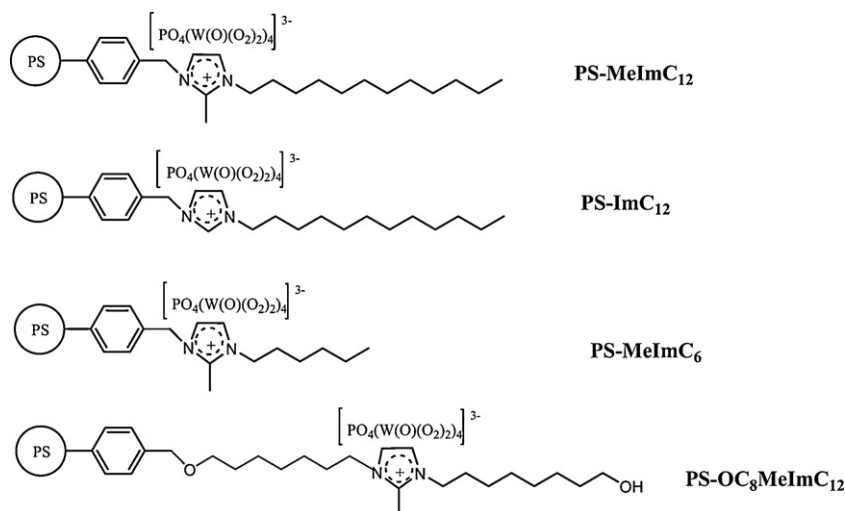


Fig. 1. Structure and name of the synthesized resins.

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 amphiphilic 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-MeImC₁₂, PS-ImC₁₂, PS-MeImC₆ 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 vacuum 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 dichloromethane, 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-OC₈MeImC₁₂ 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 dichloromethane, 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 \times 0.32 mm \times 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.

Download English Version:

<https://daneshyari.com/en/article/56364>

Download Persian Version:

<https://daneshyari.com/article/56364>

[Daneshyari.com](https://daneshyari.com)