

# Efficient Routes for Epoxidation of Monoterpenes Using Polyoxometalates

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## Introduction

The development of catalysts for selective and environmental friendly oxidation of organic compounds is an important research goal. Catalytic epoxidation of alkenes has attracted much attention both in industry and in organic synthesis, because epoxides are among the most useful synthetic intermediates.<sup>1</sup> The formation of epoxides *via* metal-catalyzed oxidation of alkenes represents the most elegant and green route for the production of this class of compounds.<sup>2</sup> Polyoxometalates (POMs), large transition metal oxygen anion complexes, have been largely used as catalysts as consequence of their unusual versatility and compatibility with eco-sustainable conditions. Transition metal substituted polyoxometalates are attractive as oxidation catalysts since they contain reactive low valence transition metal centers complexed by inorganic oxometalate ligands which may have high capacity as oxygen transfer agents.<sup>3,4</sup>

## Experimental

In the present work, we will report the epoxidation of mono-terpenes such as, geraniol, and (R)-(+)-limonene with H<sub>2</sub>O<sub>2</sub>, catalysed by derivatives of Keggin type POMs:

- i) mono-lacunar [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup>, and the tri-lacunar [PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup>,
- ii) mono-substituted [PM(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>n-</sup> with M = Co<sup>II</sup> and Fe<sup>III</sup>
- iii) sandwich type [M<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>m-</sup> with M = Co<sup>II</sup>, Fe<sup>III</sup>.

The most active homogeneous catalysts were immobilised using two different support materials:

- i) metal-organic framework (MOF)
- ii) mesoporous micelle-templated silica SBA-15.

These supports were previously functionalized with appropriate organic groups to achieve efficient immobilization (Figure 1). The stability, reusability and leaching behaviour was analysed for the heterogeneous catalysts.

POMs and the supported POMs were analyzed by FT-IR and FT-Raman spectroscopies, powder X-ray diffraction, elemental and thermogravimetric analyses. For analysis of the reaction products, FID GC and GC-MS were used.

## Results/Discussion

A systematic study has been performed to clarify the influence of the nature of transition metals incorporated in the POMs framework in the catalytic performance. The stability of the catalysts was analysed concerning the H<sub>2</sub>O<sub>2</sub> concentration and water content by UV/Vis and EXAFS spectroscopy. These homogeneous studies had as main goal the optimization of catalyst turnovers, selectivities and stabilities (Table 1).

The heterogenization of active compounds is extremely important since the catalyst can be easily separated from the reaction mixture and recycled, which is of significant industrial interest. Therefore, new heterogeneous catalysts based in POMs were prepared and their catalytic performance for the oxidation of geraniol and (R)-(+)-limonene was studied. The influence of the support as well the immobilization method will be analyzed.

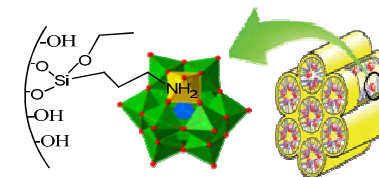


Figure 1. Covalent immobilization of POM on functionalized SBA-15.

Table 1. Catalytic results to geraniol oxidation using different POMs with H<sub>2</sub>O<sub>2</sub> in an homogeneous medium. Selectivity data for 2,3-epoxigeraniol.

POM	Time (h)	Conversion (%)	Selectivity (%)
[PW <sub>11</sub> O <sub>39</sub> ] <sup>7-</sup>	3	97	77
[PW <sub>11</sub> Fe(H <sub>2</sub> O)O <sub>39</sub> ] <sup>4-</sup>	3	50	85
[Fe <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> (PW <sub>9</sub> O <sub>34</sub> ) <sub>2</sub> ] <sup>6-</sup>	1,5	30	74
[Co <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> (PW <sub>9</sub> O <sub>34</sub> ) <sub>2</sub> ] <sup>10-</sup>	1,5	100	91

## References.

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