

Catalytic epoxidation of R-(+)-limonene using the Jacobsen's catalyst under heterogeneous conditions

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Introduction

The epoxides of R-(+)-limonene are commercially important materials for pharmaceutical, flavor and perfumery industry [1]. Jacobsen's catalyst has previously been shown to be active for the epoxidation of olefins [2]. The main disadvantage of this catalyst is related to its performance as a homogeneous catalyst, which hinders the catalyst recovery and reuse after the reaction [3]. To overcome these drawbacks, various strategies involving the immobilization of the catalyst onto solid supports have been proposed [4]. However, the immobilized catalyst usually leads to partial loss of catalytic activity as compared to its analogous homogeneous counterpart, because the chemical structure of the homogeneous complex might be distorted after the immobilization [4]. Furthermore, the loss of catalyst stability in presence of the most common oxidizing agents (NaOCl, m-CPBA and PhIO), avoids its useful reutilization [4]. An alternative strategy is to adjust the solubility of the homogeneous catalyst under reaction conditions, resulting in the direct precipitation of the catalyst [4]. In the present work, we developed a new method for the heterogeneous epoxidation of olefins using the Jacobsen's catalyst and *in situ* generated dimethyldioxirane (DMD) as oxidizing agent, without the use of any solid support. The success of this strategy will be exemplified in R-(+)-limonene epoxidation.

Materials and Methods

The Jacobsen's catalyst was prepared by refluxing ethanolic solutions of (R,R)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt and 3,5-di-tert-butyl-salicylaldehyde in a 1:2 molar ratio. The obtained ligand was complexed with manganese acetate to give the Jacobsen's catalyst [5]. The purity and chemical identity of the Jacobsen's catalyst was confirmed by FT-IR and its activity was tested in R-(+)-limonene epoxidation using *in situ* generated DMD as oxidant at room temperature. In all experiments, 2.0 mmol of R-(+)-limonene and 0.05 mmol of catalyst were used, whereas the KHSO₅ and acetone were varied. DMD is formed by reaction between KHSO₅ (Oxone®) and acetone at pH = 8.0. The reaction products were identified by GC-MS using a chiral capillary column Betadex GTA.

Results and Discussion

The experimental results showed that the Jacobsen's catalyst could be separated after reaction by decantation, when R-(+)-limonene/KHSO₅ = 0.5 and acetone/R-(+)-limonene = 2 molar ratio were used. Under these reaction conditions, diepoxides appeared to be the predominant products, along with a complete conversion of R-(+)-limonene (see figure 1). It was also observed that there was no significant decrease of the initial catalytic activity after two consecutive runs (figure 2).

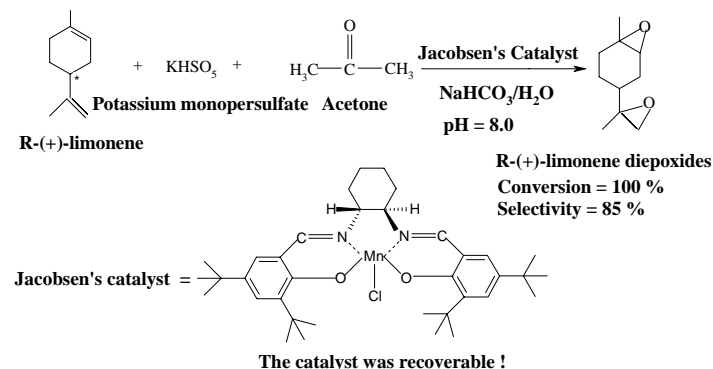


Figure 1. Reaction scheme for R-(+)-limonene epoxidation using the Jacobsen's catalyst and *in situ* generated DMD as oxidizing agent.

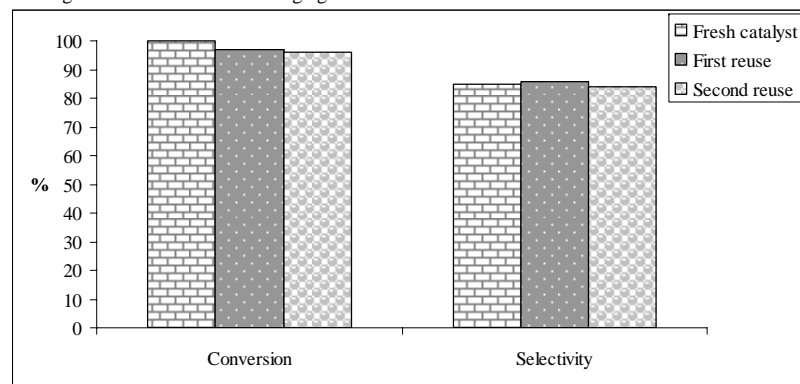


Figure 2. Stability and reusability of Jacobsen's catalyst in R-(+)-limonene epoxidation with *in situ* generated DMD as oxidizing agent.

Significance

We have demonstrated a new strategy for the heterogeneous epoxidation of olefins by adjusting the reaction conditions without the use of any solid support.

References

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