

## Ti-MCM-41 materials synthesised at room temperature as catalysts for cyclisation of ( $\pm$ )-citronellal

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### Introduction

Citronellal can be cyclised to produce isopulegol, which is an intermediate in the synthesis of menthols. These chemicals are all used in the fragrance industry and menthol is also an important product used as a flavour, a pharmaceutical and in oral care. The cyclisation of citronellal proceeds readily with various homogeneous catalysts, but the catalyst frequently cannot be recovered and reused. Several heterogeneous catalysts have also been found to be active with, for instance, Sn-Beta zeolite being highly active and diastereoselective [1].

Ordered mesoporous materials have stimulated an enormous interest in the scientific community, principally in the fields of heterogeneous catalysis and materials science, since their disclosure in 1992. The MCM-41 material is the most widely studied among the numerous mesoporous materials due to the structural simplicity. Catalytic activity can be generated by modification of the siliceous framework by heteroelements such as Ti. In previous work we have demonstrated that well structured Ti-MCM-41 materials, with good thermal and mechanical stability in air and catalytically active in the oxidation of cyclohexene, could be synthesised at ambient temperature and pressure [2,3]. In the present work we extend the applicability of those Ti-MCM-41 materials, as heterogeneous catalysts, to produce an important intermediate, isopulegol, from the cyclisation of citronellal. The use of this kind of materials appears to be a good option over homogeneous catalysts, because they offer the advantage of recovery and, consequently, contribute to environmentally friendly processes.

### Experimental

The Ti-MCM-41 samples were prepared by direct synthesis as previously reported [2]. The samples are designated by TiRpN-x where R = E or B denotes respectively, Ti(OEt)<sub>4</sub> or Ti(OBu<sup>n</sup>)<sub>4</sub>, p the propan-2-ol, N the surfactant C16 or C18TMABr and x corresponds to the nominal molar ratio Si/Ti. All samples were characterised by XRD, N<sub>2</sub> adsorption at 77K and DR UV-Vis. The catalytic reactions were carried out in a round bottom flask equipped with a septum port and a reflux condenser, under nitrogen using toluene as solvent and 15 wt.% catalyst with respect to the substrate racemic citronellal. The solvent:( $\pm$ )-citronellal volume ratio was 25. Aliquots were removed at different reaction times, and the products were analysed by a gas chromatograph equipped with a Supelcowax 10 capillary column. Diastereoisomers were identified by <sup>13</sup>C and <sup>1</sup>H NMR.

### Results and discussion

The catalytic performance of the Ti-MCM-41 catalysts, in the same reaction conditions, is displayed in Fig. 1.

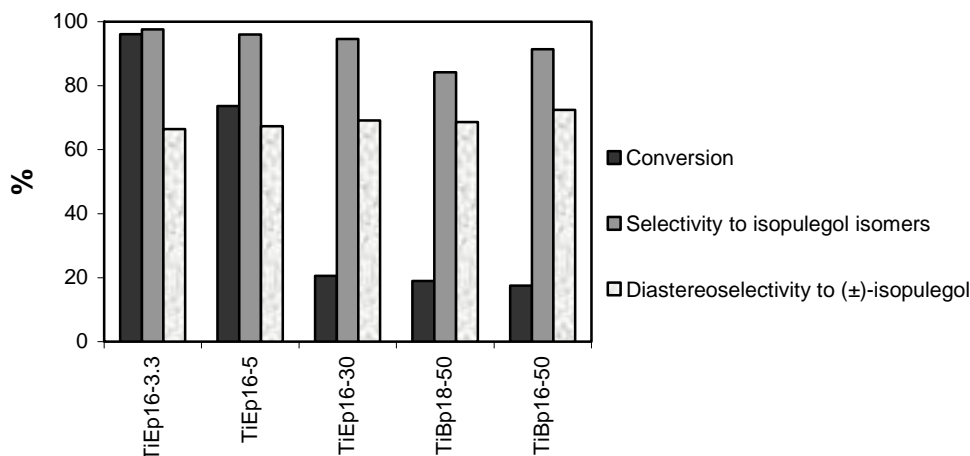


Figure 1. Conversion, selectivity to isopulegol isomers and diastereoselectivity to (±)-isopulegol for the cyclisation of citronellal over Ti-MCM-41 catalysts.

The comparison of the Ti-MCM-41 samples with different Ti content shows that the diastereoselectivity is similar, with (±)-isopulegol as the main isomers (66-72%). Comparable conversions are obtained over catalysts with Si/Ti of 30 and 50, in consistency with the similarities of their surface chemical and pore structural characteristics [2]. On the other hand, a significant increase of conversion is observed for high Si/Ti, evidencing an increase of catalytic acidic sites. A Si/Ti ratio of 3.3 is the optimal leading to a very high conversion, 96%, associated with excellent selectivity for isopulegol isomers, 98%. The present results are consistent with the properties of this catalyst, which combines catalytically active sites with a relatively good quality of the pore structure, high surface area and pore volume and uniform pore diameters in the mesopore range.

## Conclusions

This work shows that the Ti-MCM-41 materials tested are catalytically active for the cyclisation of citronellal with a good selectivity for the desired isomer. The material with higher titanium content (Si/Ti=3.3) was found to be the best catalyst. Therefore it can be concluded that the Ti-MCM-41 samples with high Ti content fulfil the requirements for a heterogeneous catalyst for the ene cyclisation of citronellal.

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