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ACCEPTED MANUSCRIPT

Pore size matters! Helical heterogeneous catalysts in olefin oxidation

Marta S. Saraiva^a, Cristina I. Fernandes^a, Teresa G. Nunes^b, Maria José Calhorda^{a*}, Carla D. Nunes^{a*}

Highlights

- Chiral MCM porous materials were synthesized (curved channels).
- Mo(II) complexes were immobilized in the chiral materials.
- The functionalized materials oxidized selectively several chiral substrates.
- The functionalized materials were reused for several runs keeping a high activity.

Abstract

Helical mesoporous materials of the MCM-41 type with different pore sizes were prepared, choosing as templates myristyl (C_{14}) or cetyl (C_{16}) trimethyl ammonium salts, and functionalized with Mo(II) active sites based on MoI₂(CO)₃ (**1**) and MoBr(η^3 -C₃H₅)(CO)₂ (**2**) fragments, respectively, using a pyridine-2-carbaldehyde ligand as anchor.

The new materials were tested as the catalytic precursors in the epoxidation of *cis*-cyclooctene, styrene, *R*-(+)-limonene, *trans*-hex-2-en-1-ol, *cis*-3-hex-1-ol, and geraniol using *tert*-butylhydroperoxide (tbhp) as oxidant. All catalysts were moderately to highly selective towards the epoxide products. The materials with larger pores (C₁₆ template) displayed a better catalytic activity, leading in general to higher conversions and selectivities, as well as faster kinetics. For instance, geraniol is epoxidized (more than 90 %) with conversions above 90 %. The major achievement of these catalysts, however, is the excellent product selectivity control, which is boosted when the allyl

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