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Ligand-stabilized homogeneous Mo catalysts for deoxydehydration reactions

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PURPOSE OF THE ABSTRACT

The global use of fossil feedstocks as the main resource for the production of energy, chemicals and materials results in several issues, most importantly global warming. While for energy needs several alternatives are available, biomass is likely the only realistic option for the sustainable production of chemicals. However, the components of biomass generally have a high oxygen functionalization degree compared to common industrial chemicals and, as a result, deoxygenation reactions are required. An interesting deoxygenation reaction is deoxydehydration (DODH), which involves the reductive removal of two vicinal hydroxy groups, resulting in formation of a double bond.[1-4] The earth abundant Mo and V have been reported as active catalysts; however, yields and activities are much lower than with the more active, but expensive, Re catalysts. Furthermore, for Mo, the effect of ligands on the metal catalyst has barely been investigated. Therefore, we have examined the effect of several β -diketonate ligands on a Mo catalyst.[5] Both an electronic and steric effect were observed, however, the latter was dominant. The bulky electron donating β -diketonate 2,2,6,6-tetramethyl-3,5-heptanedionate (TMHD) had the most positive effect, resulting in up to a ten-fold increase in yield and turn-over frequency (TOF) for the desired DODH product. The increase in yield can be explained by coordination of TMHD to Mo, which results in a steric barrier that hampers the formation of oligonuclear Mo oxo-clusters. If this clustering is allowed to continue unimpeded, it results in precipitation and, hence, deactivation of the catalyst, which is a well-known problem in Mo-catalyzed DODH. The stabilization of the homogeneous catalyst was demonstrated by filtration experiments and electrospray ionization mass spectroscopy (ESI-MS). Using the latter method, oligo- and even mononuclear Mo species were detected in the presence of TMHD, while in the absence of TMHD barely any Mo remained in solution. Finally, the positive effect of TMHD was shown to be present for several different substrates and reductants.

FIGURES

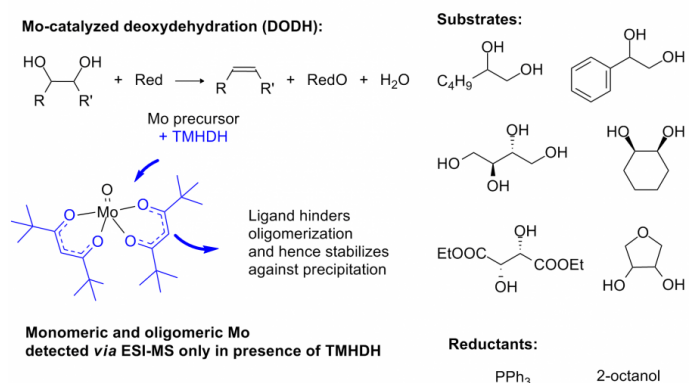


FIGURE 1

graphical abstract

2,2,6,6-tetramethylheptanedionate stabilizes homogeneous Mo in the deoxydehydration of several polyols

FIGURE 2

KEYWORDS

deoxydehydration | molybdenum | polyols | beta-diketonates

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