Deoxydehydration of polyols using rhenium-based catalysts

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PURPOSE OF THE ABSTRACT
Today new industrial processes starting from renewable feedstocks such as polyol derivatives are proposed to improve environmental conditions and to limit the use of non-renewable sources. Actually, there is a growing interest in catalytic deoxygenation methods, and especially in deoxydehydration (DODH). This reaction can remove two adjacent hydroxyl groups from vicinal diols to afford the corresponding unsaturated derivatives. Until now, the most promising catalysts for these kinds of reactions are rhenium-based [1,2]. However for industrial applications, Re is particularly expensive, not particularly green and furthermore the turnover numbers are still too low (for quantitative conversions are often necessary amouts higher that 1%). To solve the problem, two are the strategies: to lower as much as possible the amount of rhenium or to use other metals that are safer and greener. Our group is expert in preparation, characterization and use of homogeneous catalysts to hydrogenation and deoxydehydration reactions [3]. In the present contribution, we will describe a sustainable catalytic conversion of several polyols (glycerol, erythritol sorbitol) into deoxygenated derivatives like allyl alcohol, butadiene etc.. Rhenium has been the first metal taken into consideration [4] even if, in some recent experiments, vanadium and tungsten have shown promising activities.

In Figure 1 are depicted the reaction conditions with all the tested rhenium catalysts. Hydrogen atmosphere always showed a higher conversion and selectivity even if the reductant was proved to be the alcohol (solvent or reactant if in neat condition). Among the Re oxides, both ReO3 and MTO were particularly active but at concentrations around 2% while the best performances in terms of conversion and selectivity was reached when 1% of commercial Re-triphenylphosphine complexes was used.

Density functional theory (DFT) calculations were also carried out to shed more light on to the rhenium-based catalysis of glycerol DODH. In particular, the DFT study was focused on the glycerol DODH catalyzed by [ReO3?] and ReO3 and on the evaluation of two alternative pathways: glycation-reduction and reduction-glycation. The identification of active catalytic species and rate-limiting steps within the hypothesized DODH reaction pathways were the main outcomes of this theoretical investigation.
FIGURES

FIGURE 1
Figure 1
Rhenium catalysed deoxydehydration of polyols

FIGURE 2

KEYWORDS
rhenium | deoxydehydration | renewable feedstock | glycerol

BIBLIOGRAPHY