

Catalyst Recycling Using Reactive Ionic Liquids

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Abstract

Highly substituted amines are of great interest for the chemical industry since they are used as building blocks, e.g. for surfactants. Homogeneously catalyzed aminations can be conducted under milder conditions and with high selectivity towards the often-desired linear amines. The most important disadvantage of homogeneously catalyzed reactions is the often-challenging catalyst recycling, making it too expensive for industrial means. An elegant solution to this problem in the synthesis of dimethyl amine derivatives is the use of dimethyl ammonium dimethyl carbamate (dimcarb), which is obtained by the reaction of dimethylamine and CO₂. It has very promising properties, because it is predominantly present in the ionic form, yet serves as an amine source. Consequently, it can be considered a reactive ionic liquid.

The catalytic conversion of 1,3-dienes with amines to linear allylic amines is well-known. A palladium-based catalyst and the DPPB ligand is used for converting the renewable terpene β -farnesene to dimethyl amine derivatives. These farnesyl amines are interesting building blocks for nitrogen-based surfactants. The solvent-free hydroamination leads to a yield of 89% of the desired products. Furthermore, spontaneous phase separation takes place, which allows removing the non-polar product phase and reusing the polar catalyst phase. The sulfonated DPPB analogue can efficiently be immobilized in the dimcarb phase and be reused several times, increasing the total turnover number by the factor of ten. This concept also works for other 1,3-dienes, like β -myrcene and isoprene.

The telomerization is a dimerization of 1,3-dienes with an addition of a nucleophile. Applying dimcarb and 1,3-butadiene without any solvent leads to dimethyl octadienyl amines. Since the product is soluble in dimcarb, it must be extracted with cyclohexane. The catalyst is immobilized in dimcarb by using a tri-sulfonated PPh₃ ligand (TPPTS). In this way, the catalyst can be recycled more than 30 times in a row without any loss in activity or selectivity at all.

Literature

T. A. Faßbach, R. Kirchmann, A. Behr, A. J. Vorholt, *Green Chem.* **2017**, Recycling of homogeneous catalysts in reactive ionic liquid – solvent-free aminofunctionalizations of alkenes, *19*, 5243–5249.