Recycling of Phosphorous-based Organocatalysts by Organic Solvent Nanofiltration

J. Großeheilmann\textsuperscript{a}, H. Büttner\textsuperscript{b}, C. Kohrt\textsuperscript{b}, T. Werner\textsuperscript{b}, U. Kragl\textsuperscript{a,b}

**Introduction**

Several phosphorous-based organocatalysts which significantly accelerate the coupling of epoxides and \(\text{CO}_2\) with a highly atom efficient reaction under mild conditions were developed.\textsuperscript{[1]} The produced cyclic carbonates are versatile organic compounds for the synthesis of organic building blocks, alternative solvents and polymer monomers. However, the separation of the organocatalysts for a subsequent recycling is typically challenging. Herein we evaluate Organic Solvent Nanofiltration (OSN) as promising alternative providing high purities and a low energy-demanding separation process.\textsuperscript{[2]}

**Results**

**Filtration Experiments**

Screening experiments with different membranes from DM series (Evonik MET Ltd., UK) were performed. The P-catalyst was rejected with 95.4% (DM 300) and 99.1% (DM 150) respectively, which facilitates a highly selective separation of the catalyst from the product. For recycling experiments EtOH was chosen as solvent because of the highest flux (12.7 L m\(^{-2}\) h\(^{-1}\)) with the membrane DM 300.

**Catalyst and Product Separation from Postreaction Mixture**

The reaction mixture consisting of butylene oxide (0.133 mol), P-catalyst (5 mol%) and 1.0 MPa carbon dioxide was allowed to react for 8 h at 60 °C. Conversion and yield were determined prior dilution to 40 mL with EtOH (batch I) (Figure 4). Up to eleven diafiltration steps were performed and the feed solution was concentrated to an initial volume of 20 mL to flush out the product. Figure 4 presents the amount of product during the reaction / filtration cycle (green points represent the experimental data, white points represent the theoretical data). The product was rejected with 52% and isolated in high purity. To investigate the catalysts activity after the filtration steps, fresh substrates were added to the solution and the reaction was performed again. The catalyst was still fully active (up to 99% yield) after batch IV and could be easily reused after the nanofiltration steps. For all experiments the same membrane (DM 300) was used and shows a good long-term stability with 44 filtration steps.

**Conclusion**

With this study we illustrate OSN as an eco-friendly alternative separation technology to existing methods for product and catalyst separation. The membrane screenings show high rejection rates (>99.1%) for the catalyst. With the separation experiments we isolated the product in high purity without further purification steps. At the same time the catalyst was reused without any loss of activity. Furthermore bifunctional phosphonium salts were synthesized and used as organocatalysts for the synthesis of cyclic carbonates from \(\text{CO}_2\) and epoxides.

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\textsuperscript{a} Institute of Chemistry | University of Rostock | Albert-Einstein-Str. 3a | 18059 Rostock | Germany

\textsuperscript{b} Leibniz Institute for Catalysis | Albert-Einstein-Str. 29 a | 18059 Rostock | Germany

References: