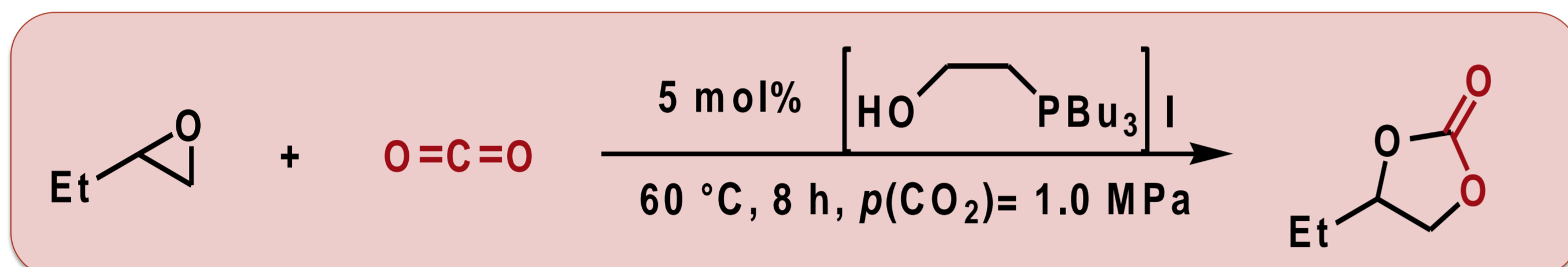


Recycling of Phosphorous-based Organocatalysts by Organic Solvent Nanofiltration

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Introduction

Several phosphorous-based organocatalysts which significantly accelerate the coupling of epoxides and CO₂ with a highly atom efficient reaction under mild conditions were developed.^[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.^[2]



Scheme 1. Phosphorous-based organocatalyzed synthesis of butylene carbonate.

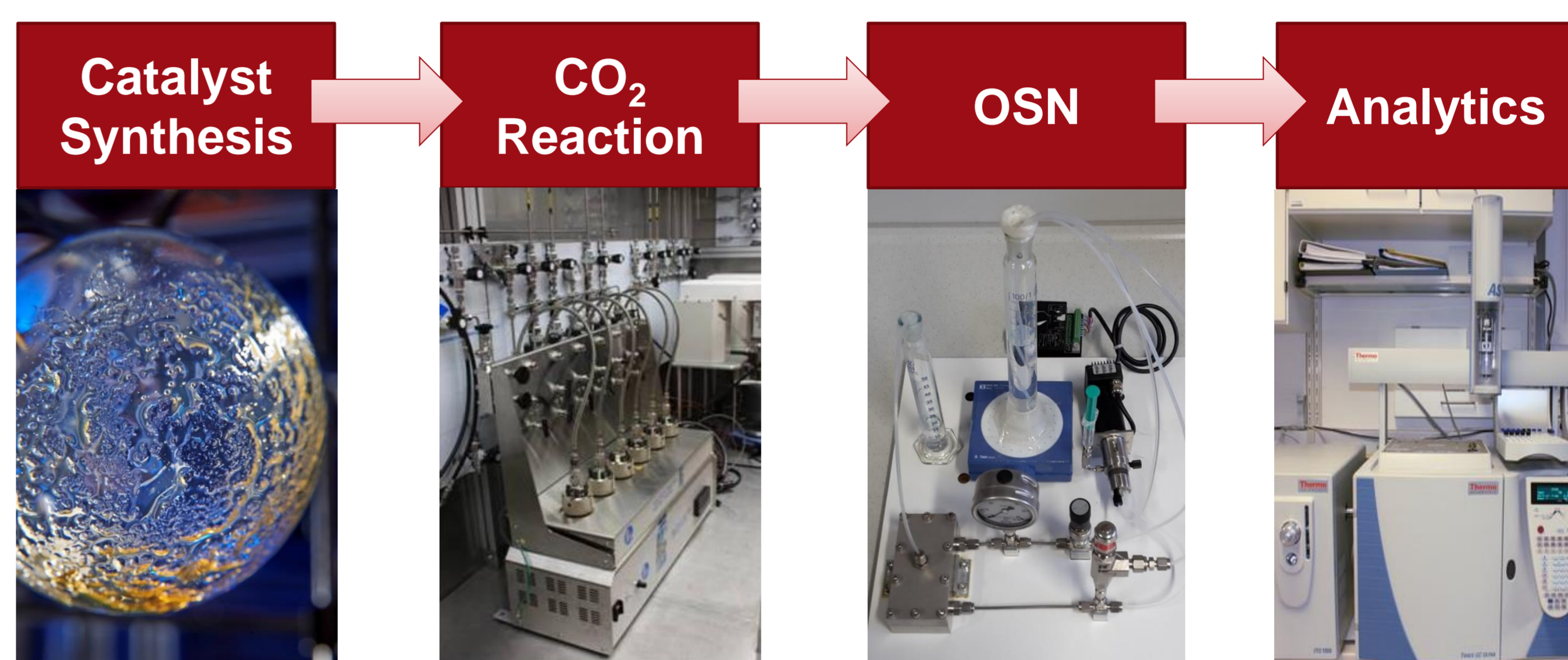


Figure 1. Scheme of the working process, used in this study.

Results

Instrumental Setup

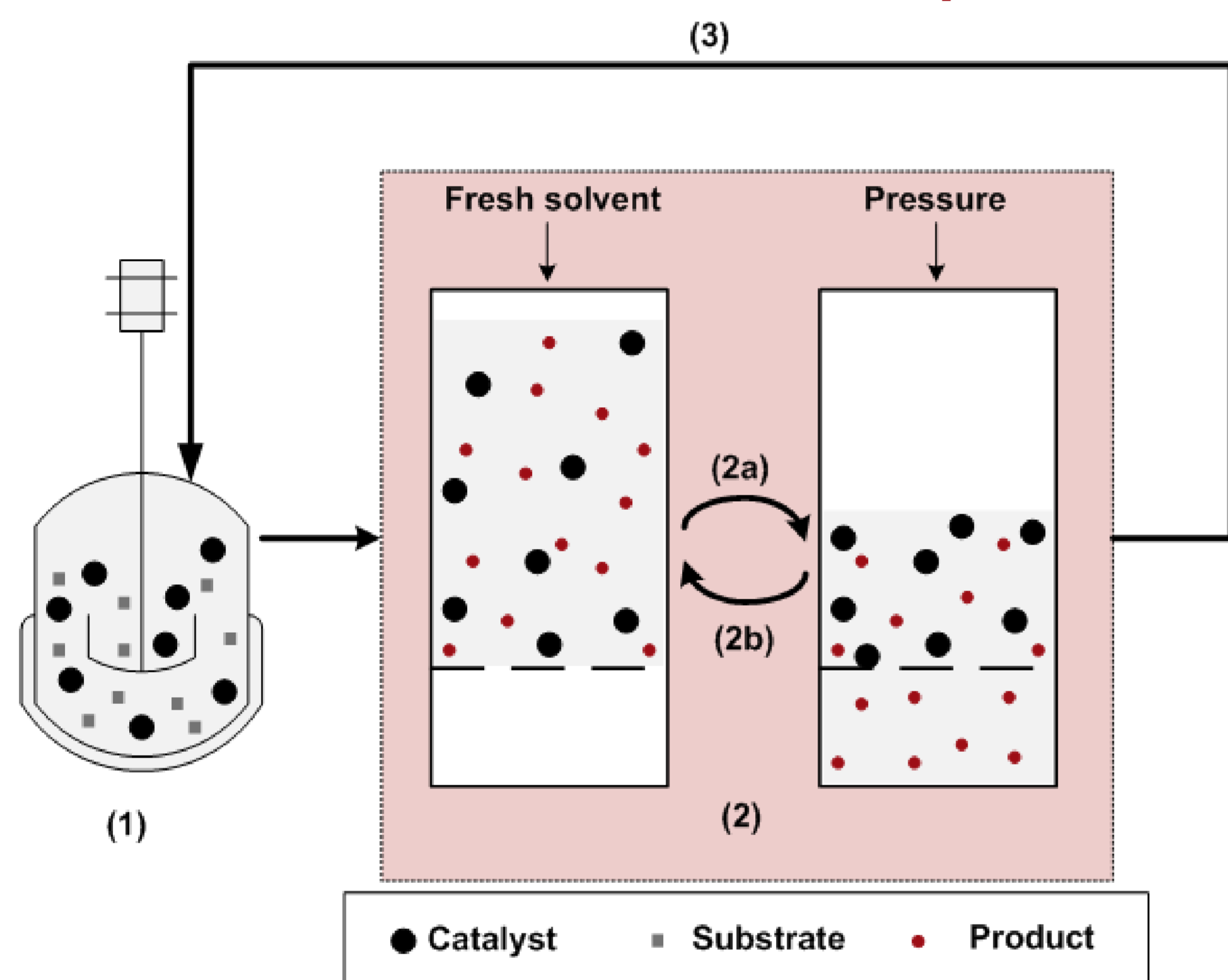


Figure 2. Process scheme for the reaction / diafiltration cycle in the cross flow cell: (step 1) reaction of butylene oxide with carbon dioxide to butylene carbonate; (step 2) discontinuous diafiltration of the diluted postreaction mixture (first batch from reaction vessel); (step 2a) repeated filtration; (step 2b) repeated dilution; (step 3) addition of fresh substrates.

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.

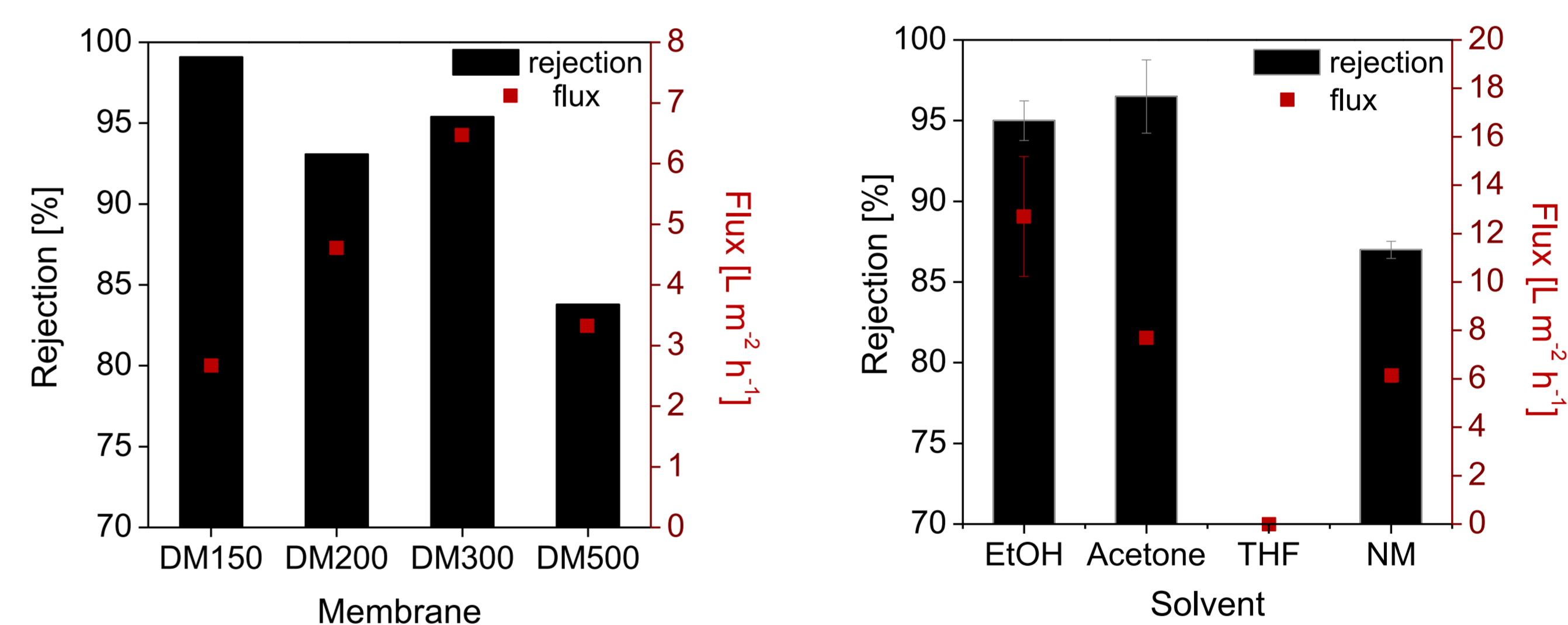


Figure 3. Filtration results with different membranes (left). Conditions: 0.15 M P-catalyst in EtOH, 30 bar, $\vartheta = 25$ °C, stirred cell, $n = 2$. Filtration results with different solvents (right). Conditions: DM 300, 20 bar, $\vartheta = 25$ °C, cross flow cell, 70 mL min⁻¹, 0.15 M P-catalyst in solvent, $n = 2$, NM = nitromethane.

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.

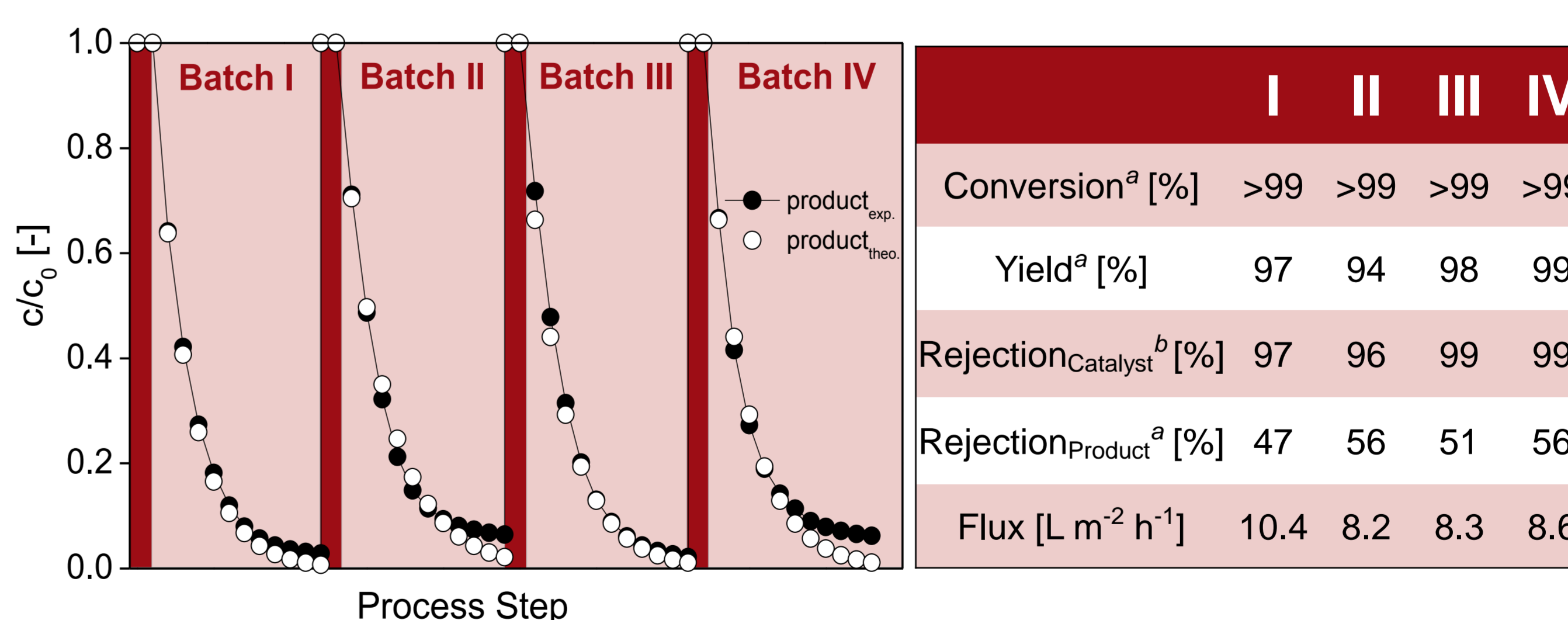


Figure 4. Concentration of the product in the filtration cross flow cell during different reaction batches and diafiltration steps (11 diafiltration steps after each batch). I-IV denote the reaction batches. ^aDetermined by GC/MS measurements. ^bDetermined by ³¹P-NMR measurements with an internal standard.

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 CO₂ and epoxides.

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