Continuous processes for the Rh-catalyzed carbonylation of olefins and unsaturated esters enabled by cyclodextrin-mediated aqueous biphasic systems

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Abstract

Sustainability and efficiency are two crucial values in the chemical industry. One strategy to reach these goals in homogeneous catalysis is the use of environmentally benign solvents in the development of novel, efficient production processes. A successful example is the Rh-catalyzed carbonylation in an aqueous-organic two-phase system. While separation of the aqueous catalyst phase and apolar products is accomplished very effectively, the approach is limited by the solubility of the substrates, which especially holds for long-chain substrates. The resulting need for an intensification technique has long been an area of research that has received great attention. The use of cyclodextrins (CD), cyclic oligosaccharide molecules that form conical cylinders with a hydrophilic surface and a hydrophobic cavity, as mass transfer agents represent a promising avenue for the success of such aqueous biphasic systems (Figure 1, left). Their implementation leads to a potentially economically competitive trade-off between reaction activity and catalyst retention.

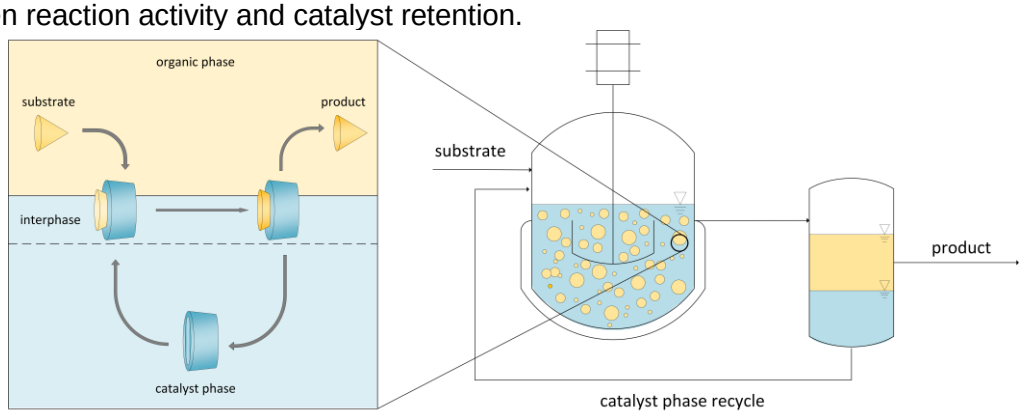

Figure 1: Working principle for cyclodextrin-mediated reaction systems (left). Process design for the recycling of homogeneous catalysts using aqueous biphasic systems (right).

We investigated these reaction systems in a continuous operated miniplant (Figure 1, right) for hydroformylation and hydroaminomethylation (one-pot auto tandem reaction of hydroformylation followed by reductive amination) reactions. After preliminary batch experiments, optimization of different reaction parameters was carried out during continuous operation. At high selectivity's of 80% and yields above 70%, on average only 0.15 mg Rh per kg of main product was lost via the product stream. With such extremely low loss of 0.003 % h-1 of the initial Rh mass (0.24 % overall), being the lowest leaching value ever reported for the HAM at this scale, industrial application comes into reach.