Continuous Flow Ruthenium-catalysed Hydrogen-transfer Methods

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Introduction
Oxidations and reduction processes are pivotal reactions in chemical synthesis and industrial processes. The development of selective, safe and practical methods continues to drive major interest in the scientific community. Catalytic methods have special importance in large-scale industrial processes, in that perspective hydrogen-transfer systems represent an attractive approach towards selective catalytic transformations.

Oxidation of Secondary Alcohols
General procedure:

The studied system used acetone as solvent and hydrogen acceptor, dichloro(p-cymene)ruthenium(II) dimer as a cheap, readily available catalyst and triethylamine (Figure 1).¹ The ability to work with higher pressures in continuous flow allowed acetone to be used in higher temperatures.

Scope:

Scale-up:

Reduction of Aromatic Nitriles
General procedure:

The method developed for the reduction of nitriles to primary amines requires no additives, and uses isopropanol as both solvent and reducing agent. It utilizes 1 mol% of the commercially available [Ru(p-cymene)Cl₂]²⁻ and has a residence time of ca. 9 min with throughput of 50 mmol/h.

Scope:

Conclusions
In summary we have developed a continuous flow system for the ruthenium-catalysed Oppenauer-type oxidation of mainly secondary alcohols, and for the reduction of aromatic nitriles to primary amines. The platform utilizes 1 mol% of a cheap and commercially available ruthenium catalyst, and acetone/2-propanol as hydrogen acceptor/donor. The system was successfully applied to a range of different substrates.

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References
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