Review

Catalyst retention in continuous flow with supercritical carbon dioxide

S.C. Stouten, T. Noël, Q. Wang, V. Hessel *

Laboratory of Chemical Reactor Engineering/Micro Flow Chemistry and Process Technology, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

ABSTRACT

This review discusses the retention of organometallic catalysts in continuous flow processes utilizing supercritical carbon dioxide. Due to its innovative properties, supercritical carbon dioxide offers interesting possibilities for process intensification. As a result of safety and cost considerations, processes that use supercritical carbon dioxide are preferably done in continuous flow, as they require a pressure upwards of 74 bar. Many of the reactions that benefit from the application of supercritical carbon dioxide also involve the use of a homogeneous catalyst however, requiring efforts to recycle the catalyst when these are applied in continuous flow. Alternatively, the catalyst may be retained in the reactor by modifying the process or catalyst, such as by catalyst immobilization, membrane separation, or biphasic processing exploiting the properties of supercritical carbon dioxide. Each of these methods is discussed, including their advantages and drawbacks. Also discussed are milli- and micro-flow processes and their possibilities for integrated catalyst retention and handling supercritical carbon dioxide.

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1. Introduction

Typically, the use of solvents in chemical processes is a necessary evil. Solvents inevitably lead to waste, yet are often required either as a medium for a chemical reaction or for downstream separation [1,2]. Particularly separation and purification require large amounts of solvent. In some processes, reducing or eliminating the use of solvents may be a possibility, but in most cases this is not an option. Alternatively, green solvents may be employed, such as supercritical carbon dioxide (scCO$_2$), which is cheap, nonflammable

and non-toxic [3–6]. In addition, at depressurization scCO$_2$ will revert to a gas, meaning no solvent residue will remain to contaminate the final product. An example of a well-known industrial process in which these advantages are exploited is the extraction of caffeine from coffee beans [7].

Beyond this however, the use of an innovative solvent such as scCO$_2$ also provides opportunities for process intensification. At supercritical conditions, above 73.9 bar and 304.25 K, the properties of carbon dioxide are somewhere in between that of a gas and a liquid. As a result, scCO$_2$ has a high solvent power, high diffusivity and can accelerate gas–liquid reactions by allowing operation under single phase conditions [8]. Additionally, around the supercritical point these properties change rapidly with temperature and pressure, which provides interesting opportunities. For example,

* Corresponding author.
  E-mail address: v.hessel@tue.nl (V. Hessel).

small adjustments in process conditions may result in large changes to the solubility of dissolved species to allow separation. Of course, such advantages are best exploited when process conditions can be controlled and fine-tuned to the reaction, as is the case in continuous flow processes. In addition, operation in a continuous process avoids the use of large pressure vessels that would be required for batch production, which are undesired due to safety issues and high costs.

Still, the use of $scCO_2$ as a solvent also comes with a price tag. While CO_2's critical pressure is fairly low, compression is nevertheless energy intensive and this energy is lost upon depressurization. Hence, $scCO_2$ should be applied in processes in which it provides a distinct benefit, as was suggested by Han and Poliakoff [9]. Important reactions that have been shown to benefit from the use of $scCO_2$, such as hydroformylation and asymmetric hydrogenation, rely on the use of expensive homogeneous catalysts. Therefore, improving the performance of such catalysts by use of $scCO_2$ is particularly worthwhile.

However, as was just argued, $scCO_2$ is best applied in a continuous process, as are the aforementioned processes. For homogeneous catalysts, which are dissolved in the reaction mixture, this means a method for either catalyst recycling or retention has to be found. The goal of such retention methods is to extend the use of the organometallic catalyst beyond that of a single pass through the reactor, effectively increasing the catalyst's turnover number (TON). Several approaches to this have been developed, for instance by catalyst immobilization [10,11], membrane reactors [12,13], biphasic processes [14], or by a down-stream separation exploiting the properties of $scCO_2$ [15]. The aim of this review is to provide an overview of these approaches for catalyst retention in $scCO_2$ processes.

2. Systems using catalyst immobilization

Possibly the most obvious approach to achieve catalyst retention is by the immobilization of an organometallic catalyst onto a solid support, thereby creating a heterogenized version of the catalyst [10,11]. Through one of its ligands, the organometallic catalyst is anchored to a support material. In most cases, catalytic performance suffers from this modification of the existing catalytic complex, although the mobility and performance of the immobilized catalyst can be improved by using a spacer between ligand and support. Catalyst leaching is an issue that may occur if the metal centre dissociates from the ligand to which it is anchored, which is why the use of multi-dentate ligands is preferred. It should also be noted that the "heterogenized" organometallic complex will be nowhere near as robust as a true heterogeneous catalyst.

Although the use of $scCO_2$ offers many advantages, many homogeneous catalysts are poorly soluble in $scCO_2$ by themselves. To overcome this, catalysts are often modified achieve better solubility [16–19]. However, this does not address the catalyst retention problem for continuous flow systems. Instead, the catalyst could be immobilized on a support material, allowing both a better distribution of the catalyst over the reactor and the retention of the catalyst.

Application of an immobilized cobalt complex was investigated by Lu et al., for the conversion of CO_2 and ethylene oxide to ethylene carbonate under supercritical conditions, see Fig. 1 [20]. In the course of this reaction, the product that is formed will create a second phase which can dissolve the homogeneous catalyst, leaching it away from the supercritical phase and causing loss of activity [21]. This limitation was overcome by immobilizing the catalyst on a support, improving mixing with the supercritical phase. In addition, the immobilized catalyst could be used in continuous flow for 24 h without loss of activity. A conversion of 86% was achieved, with no formation of by-products.
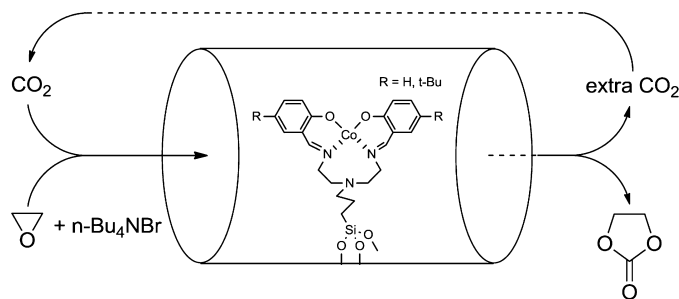

Fig. 1. Continuous cycloaddition of CO_2 over an immobilized cobalt complex. Redrawn from Lu et al. [20].

In the industrial hydroformylation process, catalyst separation is an important issue, particularly for reactions involving alkenes that are longer than 6 C atoms [22]. While for shorter alkenes catalyst and product can be separated by distillation, the thermal sensitivity of the catalyst limits this approach to products with a relatively low boiling point. Another approach is the use of an aqueous biphasic process; yet again this process is not feasible for longer alkenes, due to their low aqueous solubility. Meehan et al. investigated the continuous hydroformylation of 1-octene in $scCO_2$ by using a silica-immobilized rhodium catalyst, see Scheme 1 [23]. At 80 °C, the observed turnover frequency (TOF) in $scCO_2$ was 117 h^{-1}, which was much higher than for the batch reaction in toluene (TOF = 35 h^{-1}), but lower than observed with a free homogeneous catalyst (TOF = 283 h^{-1}). Performance of the catalyst was shown to be stable over 30 h, with no detectable rhodium leaching (<0.2%). Utilizing a controlled two-step depressurization of the CO_2, about 90% of the 1-octene could be removed from the product. In work by Bronger et al., when a catalyst with a phenoxaphosphino-modified Xantphos-type ligand was used, see Fig. 2, catalyst stability was improved in $scCO_2$, but no activity enhancement was observed [24].

Asymmetric hydrogenation is an important tool for selective production of specific enantiomers, used in, for example, the production of pharmaceuticals such as L-DOPA [25]. However, while hydrogenation is also possible over a heterogeneous catalyst, the enantioselective hydrogenation can only be achieved by use of a homogeneous catalyst. Asymmetric hydrogenation of dimethyl itaconate with an immobilized rhodium catalyst was investigated by Stephenson et al., revealing stable performance up to 100 °C [26]. After further optimization of the ligand, an enantiomeric excess (ee) of over 80% could be obtained, which even exceeded reported values for hydrogenation with a free homogeneous catalyst in batch [27].

While the most common approach to immobilization is by anchoring the catalyst through a covalent bond, alternative methods exist, such as by encapsulation of the catalyst. In this approach, instead of utilizing a covalent bond for immobilization, the catalyst is bound by trapping it inside the support structure. Leeke
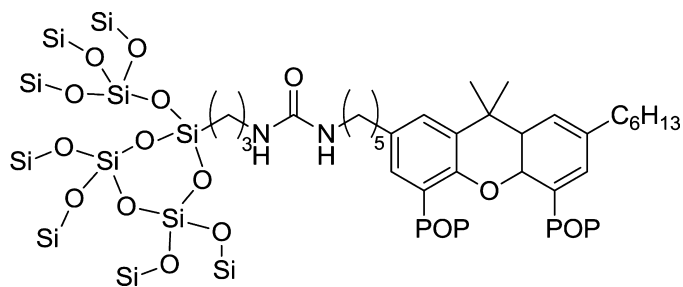

Fig. 2. Silica-immobilized ligand with a spacer used to anchor a hydroformylation catalyst.
Redrawn from Bronger et al. [24].