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7.2
State-of-the-Art

Stefan Mecking

First studies on the recovery of transition metal catalysts bound to soluble polymers were already being reported in the 1970s [1]. At the time, hydroformylation and hydrogenation with polystyrene-bound complexes of rhodium and other metals was being studied. The principle of ultrafiltration recovery was demonstrated. This first pioneering work, carried out in academia, received little attention. Only in the second half of the 1980s did the first publications on the topic begin to appear again [2]. Today, a broad range of reactions comprising carbonylations and other C–C linkage reactions, C–C coupling of aryl halides and other reagents, catalytic oxidations, and hydrogenations have been reported with polymer-bound soluble catalysts [3, 4]. Some of these reactions have also been performed enantioselectively. Generally speaking, catalyst activities and selectivities are comparable to those of homogeneous analogues that are not polymer-bound. With much of this work having been carried out in academia, actual catalyst recovery and recycling have been investigated and reported only in a portion of this expanding body of literature, and most often solvent precipitation, a method that is rather unattractive beyond small-scale laboratory batch experiments, has been employed.

Catalysts based on a variety of linear, and since the mid-1990s also highly branched, dendritic polymers, have been studied. For a large part, the polymer-bound ligands for catalysis have been prepared from commercially available polymers by polymer-analogous reactions (see Section 7.1.2) with only one or two synthetic steps.

Industrial interest in soluble polymer-bound catalysts has been closely linked to the development of ultrafiltration membranes with sufficient long-term stability in organic solvents. Membranes fulfilling these requirements were prepared first in the late 1980s. Today, solvent-stable flat sheet membranes and membrane modules are available from several suppliers. As for the viability of ultrafiltration in organic solvents, rhodium-catalyzed hydroformylation of dicyclopentadiene with continuous catalyst recovery and recycling has been demonstrated successfully on a pilot plant scale over an extended period of time [5]. The synthesis of other fine chemicals by asymmetric reduction and other reactions has also been carried out in continuously operated membrane reactors (also cf. Section 7.5) [6–9]. The extent of commercial interest in catalysts bound to soluble polymers appears to fluctuate at intervals. Amongst other factors, the price of precious metals can be a driver.

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