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Recovery and recycling of homogeneous catalysts: silica as temporary or permanent support

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Summary

Homogeneous catalysts, usually organometallic complexes of transition metals, have the advantage that they can easily be modified by changing the ligand and, after optimization, they generally display high activity and selectivity. However, the difficult and expensive recovery and recycling of homogeneous catalysts, a problem that is not an issue for heterogeneous systems, hamper their commercialization. The most common techniques for catalyst recovery that have been reported are usually accompanied by general drawbacks like incomplete complex recovery, decomposition of the catalyst leading to its deactivation, and/or tedious and costly procedures. Therefore, the search for concepts that enable the combination of the advantages of both homogeneous and heterogeneous catalysis continues as it potentially could lead to the development of highly active and selective recyclable catalytic systems.

In *Chapter 1* several strategies for the recovery and recycling of homogeneous catalysts, which have been explored and applied successfully, are discussed. Among them the discussion focus mainly on 1) biphasic catalysis, including aqueous biphasic systems, fluorous biphasic systems, supercritical fluids, and ionic liquids, 2) supported-liquid phase catalysis, both aqueous and ionic liquids supported on inorganic supports or polymeric matrixes, 3) the covalent and the supramolecular anchoring of homogeneous transition metal catalysts on organic and inorganic polymeric supports, and 4) novel strategies such as the Reverse Flow Adsorption (RFA) technology. In spite of the huge efforts dedicated to the investigation of the recovery and recycling of homogeneous catalysts, there are only a limited number of industrial applications that use such systems, mainly because of catalyst loss, and declining rates and selectivities.

The supramolecular anchoring of homogeneous transition metal catalysts on solid supports has shown to be suitable for various homogeneous catalysts. In *Chapter 2* is described a system for the recovery and recycling of chiral homogeneous

transition metal catalysts, based on supramolecular interactions (*i.e.*, hydrogen bonds and ionic interactions) between functionalized homogeneous catalysts and solid support, functionalized with complementary binding motifs, which was developed and applied in asymmetric catalytic transformations. The binding motif on the ligand significantly influences the performance in catalysis by 1) decreasing the activity when applied in the rhodium asymmetric hydrosilylation of acetophenone, 2) increasing the selectivity in the rhodium catalyzed asymmetric hydrogenation of α -methyl acetamido acrylate, and 3) by promoting the formation of multinuclear species instead of mononuclear complexes when applied in the Pt/Sn catalyzed asymmetric hydroformylation of styrene. The catalysts studies so far, however, appeared not sufficiently stable for catalyst recycling. Although the binding motifs showed to be very efficient in terms of retention of the catalyst on the support, the final efficiency achieved in catalysis is strongly dependent on the process and on the metal species used. This suggests that for each reaction the applicability of the binding motif should be re-evaluated.

Similar supramolecular strategies, in which the catalyst is temporarily attached to the support using a combination of complementary hydrogen bonds and ionic interactions, were investigated as a tool for the recovery and recycling of homogeneous transition metal catalysts using the Reverse Flow Adsorption (RFA) technology (*Chapter 3*). The RFA concept combines an adsorptive separation of the homogeneous catalyst with the reverse flow technology. The association (in solution) and adsorption (on support) of new functionalized host materials and phosphine guest ligands, functionalized with the complementary binding motifs, was fine-tuned for the application of these materials in a RFA reactor. The RFA technology for the process integrated recycling of homogeneous catalysts using these tailor-made phosphine ligands and silica-supported host materials resulted in a stable catalytic semi-continuous system. Rhodium catalyzed asymmetric hydrogenation of methylacetamidoacrylate and asymmetric hydrosilylation of acetophenone were studied as model reactions. Depending on the catalytic process the metal complex could be recycled several times without significant loss of the precious metal species or activity. The kinetics of the adsorption should be further improved to make this strategy interesting for commercial applications.

Immobilization of catalysts on a solid support is a frequently used strategy for the recovery and recycling of homogeneous transition metal catalysts, but the general

drawback is a lower catalyst activity and selectivity. A new strategy to monitor catalyst immobilization by imaging with two-photon fluorescence microscopy at the sub-micrometer level was therefore investigated (*Chapter 4*). To this end a diphosphine ligand with intrinsic fluorescent properties, which gives rise to active and selective rhodium hydroformylation catalysis was immobilized on a glass surface using traditional methods. The imaging of the immobilized ligand uncovered clustering of the ligands and therefore of the catalyst particles, explaining part of the deterioration of the catalyst compared to the homogeneous phase system. The cluster formation appears to be general and commences in solution after which the clusters are covalently attached to the solid support. Based on these results a simple new immobilization process was developed that did not give rise to clustering of the supported rhodium catalysts. Interestingly, the supported catalyst gave activities and selectivities that are close to the homogeneous catalyst, with the advantage that separation and recycling can be done by simple filtration processes.

A similar rhodium-diphosphine complex, based on Xantphos-type ligands, was anchored successfully on mesoporous silica SBA-15 to study the effect of confinement by an inorganic support in catalysis (*Chapter 5*). The performance of the immobilized transition metal complex was investigated in the Rh-catalyzed hydroformylation of 1-octene and compared to that of the complex supported on disordered amorphous silica and its homogeneous analogue. Remarkably high activities were obtained for the SBA-15 supported catalyst, which even exceeded its homogeneous analogue under certain conditions.

The various techniques to address the recovery and recycling of homogeneous transition metal catalysts investigated in this work showed to be, except for some cases, very successful. Homogeneous transition metal catalysts can be recovered and recycled keeping, and in some cases exceeding, the good/excellent catalytic performance of their homogeneous analogues. Further studies should provide a detailed insight in the interesting effects observed, and implementation of these strategies in commercial processes also requires more detailed investigations and optimization.