Tailor-made Catalysts Immobilised on Silica.
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Citation for published version (APA):

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Evaluation

The main objective of this research project has been the development of catalyst systems that combine a good catalyst performance with a quantitative separation and reuse of the catalyst. The main strategy explored and described in this thesis was directed to the immobilisation of tailor-made homogeneous catalysts on a polymeric support. Suitable homogeneous catalysts were selected based on their performance in solution and their high metal to ligand bond strength. Silicate materials were selected as the best suited materials to support these catalysts (Chapter 1).

Rhodium-diphosphine complexes, containing a large P-Rh-P bite angle, were immobilised on a polysilicate surface via several approaches: a water-soluble rhodium-diphosphine complex was immobilised as a Supported Aqueous Phase Catalyst (Chapter 2) and a trimethoxysilane functionalised rhodium-diphosphine complex was covalently anchored in a sol-gel matrix (Chapter 3) or tethered to the surface of commercially available silica. These systems were applied in the hydroformylation of 1-octene in consecutive catalytic runs. A high overall selectivity for the linear aldehyde (~ 95%) was observed using these systems under the proper conditions, which is similar to what was previously obtained using the homogeneous analogous systems. Moreover, the catalyst activity and selectivity remained unaltered upon multiple recycling while no catalyst leaching was observed.

The nature of the covalently anchored hydroformylation catalyst and the influence of the support on the catalyst were investigated by means of solid state characterisation techniques (Chapter 4). It was observed that, under standard conditions, a hydroformylation and a hydrogenation catalyst co-operated on the support. This phenomenon was exploited in a clean, one pot reaction of 1-octene to 1-nonanol via a hydroformylation-hydrogenation cascade reaction. Small manipulations in the reaction conditions affecting the catalyst-support interactions controlled the catalyst function; the catalyst could be modulated reversibly between hydroformylation, hydrogenation and hydroformylation-hydrogenation cascade reactions. As a result the conversion of 1-octene to nonanal, nonanol or octane as well as the conversion of nonanal to nonanol were all applied on one and the same batch of catalyst.

The ease of catalyst-product separation of the immobilised hydroformylation catalyst was exploited in a continuous flow reactor using supercritical carbon dioxide as the dynamic phase (Chapter 5). The system appeared to be highly active and selective for many hours without any trace of catalyst leaching or deactivation.

A catalyst-containing rotating device was developed by immobilising the hydroformylation catalyst in the channels of monoliths that were fixed in the blades of a mechanical stirrer (Chapter 6). Hydroformylation reactions were successively performed using different substrates in organic, aqueous and gaseous phases using the same batch of
catalyst. Numerous different experiments were performed on a single batch of catalyst that was used for over half a year without a notable deterioration of the catalyst performance.

Novel asymmetric transfer hydrogenation catalysts were immobilised on silica and were subsequently applied in batch and flow reactors (Chapter 7). An immobilised chiral ruthenium aminoalcohol complex showed a high activity and enantioselectivity in the reduction of acetophenone. Under optimised conditions the ee was as high as 90% at 95% conversion and a very constant catalytic activity was observed in a continuous flow reactor for over a week. Furthermore, silica appeared to be a suitable support for the solid phase synthesis of this type of catalysts and it rapidly gave access to a small series of supported ruthenium aminoalcohol complexes that generally showed product distributions that were comparable to their homogeneous analogues.

The covalent immobilisation of palladium phosphine complexes on silica appeared to be a viable method for the preparation of recyclable allylic alkylation catalysts (Chapter 8). Both bidentate and monodentate phosphine ligands formed stable palladium complexes that were recycled without catalyst deterioration. A pre-modification of the silica surface using dichlorodimethylsilane was found necessary for a good recovery of the catalyst performance upon recycling these systems. The regioselectivity of the immobilised catalysts for the alkylated products showed the same trend as the homogeneous analogues.

From the work, described in this thesis, it can be concluded that the immobilisation of tailor-made homogeneous catalysts on polysilicate supports can give rise to catalyst systems that unite a good catalyst performance with a quantitative separation and reuse of the catalyst. The anchoring of properly selected homogeneous catalysts to silicate supports gave rise to sustainable catalyst systems for hydroformylation, hydrogenation, asymmetric transfer hydrogenation and allylic alkylation reactions. In all systems the selectivity of the immobilised catalysts was the same as their homogeneous analogue and the activity was only moderately lower while no significant catalyst leaching or deterioration was observed upon recycling.