Abstract

This thesis deals with a stepwise synthesis of two unsymmetrical silica supported salen ligands. Based on one of these ligands immobilized (salen)Mn(III)- and (salen)Co(III) catalysts were synthesized and used in the asymmetric epoxidation of olefins and the hydrolytic kinetic resolution of unfunctionalised epoxides respectively. The heterogenized manganese complex showed reaction rates and selectivities in the epoxidation of olefins comparable to those of the homogeneous Jacobsen catalyst. As a disadvantage a considerable decrease in performance was observed with the immobilized catalyst in a reuse experiment. In contrast to the high catalytic activity of the anchored manganese complex, the cobalt catalyst showed only poor results, which is attributed to the site isolation of the catalytic centers.

In addition to the immobilization of these salen ligands the anchoring of a P/P chelate ligand on the silica surface was studied. Unfortunately it was impossible to succeed in the synthesis of this ligand, because of the high oxygen affinity of the trivalent phosphorus.

To investigate the products of the solid state reactions HR/MAS NMR and DRIFT spectroscopy were used. In combination with the synthesis and characterization of suitable model compounds detailed structural information of the anchored molecules were obtained. The new spectroscopic approach of dissolving the modified silica samples in aqueous sodium hydroxide (20 %) and measuring highly resolved NMR spectra could also successfully be used to identify the silica supported products.

The anchoring of the ligands on the silica surface was achieved by means of hydrolytically stable Si-C bonds. For these purposes the silica samples were chlorinated with thionyl chloride and afterwards converted with an alkenyl Grignard reagent. After the silanisation of the remaining reachable silanol groups with chlorotrimethylsilane, the alkenylated silica was hydrosilylated in the next step with 1,4-(bisdimethylsilyl)benzene. This reaction only results in a conversion of one SiH group of the bifunctional silane, so that the heterogenized SiH groups could be used for the further reactions on the silica surface.

The synthesis of the salen ligands was continued by a hydrosilylation of 4-vinylbenzyl-chloride or 3-*tert*-butyl-2-hydroxy-5-vinyl-benzaldehyde with the SiH intermediate. To modify the silica with benzaldehyde functions, which are essential for the build up of the salen ligands, the benzylchoride functionalized silica was converted with 3-*tert*-butyl-2,5-dihydroxy-benzaldehyde. In the end, both benzaldehyde modified silica samples were successively reacted with 1,2-diaminocyclohexane and 3,5-di-*tert*-butyl-2-hydroxy-benzaldehyde to yield salen functionalized silica.

The synthesis of the P/P chelate ligand also starts with a hydrosilylation reaction of the SiH functionalized silica. 2-bromo-1-methoxy-4-vinyl-benzene was successfully tethered by this reaction. But the following conversion of the bromine function with *n*-butyl lithium and diphenylchlorophosphane did result in a mixture of various products, containing the desired product only to a low content.