Abstract

This thesis deals with reactions on silica surfaces. Products on the surface are characterized by one and two dimensional HR-MAS-NMR-spectroscopy. Synthesis and NMR-spectroscopic analysis of suitable model compounds in solution prove to be very helpful to identify molecules bound to silica. These analytic tools facilitate controled synthesis on the silica surface.

At first, reactions converting surface silanol groups to other functional groups are investigated. On this purpose the influence of adsorbed water on the silanisation with chlorosilanes is studied. New approaches to bind molecules to the silica surface are the dehydrogenative coupling and the rearrangement of siloxanes. Another method to modify silica is chlorination creating Si-Cl groups, which enable further reactions. There are convincing indications of a successful reaction of ethynylmagnesium bromide with Si-Cl functions on the surface, although it can´t be unambiguously proved.

The attachment of allyl groups by allylmagnesium bromide is very reliable and effective. Subsequent reactions of the olefine permits systematic synthesis of molecules bound to the surface by Si-C bonds that are stable against hydrolysis. To avoid undesired side reactions residual silanol groups are protected by silanisation with trimethylchlorosilane. Hydrosilylation of the olefine with 1,4-bis(dimethylsilyl)benzene is used to establish Si-H functions for further reactions. The reaction conditions are optimized to reduce dehydrogenative coupling occuring as side reaction. In a following step 4-bromostyrene is successfully reacted with the Si-H function, introducing an aromatic bromine functionality. In contrast 4-iodostyrene delivers low yields.

Although model reactions in solution are successful the substitution of the attached aromatic bromine by diphenylphosphine groups forming a potential complex ligand fails both, by lithiation and palladium catalysed P-C coupling. As future task, starting from the allyl group or the Si-H function other routes to introduce phosphines can be developed.