

Preparation and Characterization of a Silica Gel Supported Zirconium(IV) Complex

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Abstract

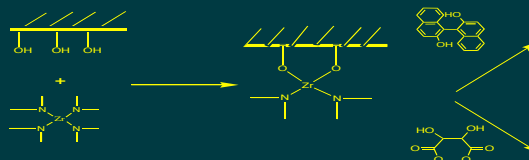
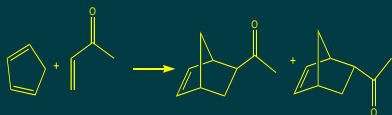
The immobilization of chiral complexes supported on silica gel to form a heterogeneous chiral Lewis acid catalyst for the [4+2] cycloaddition is our main focus. Currently, amorphous silica gel dried at 100°C and 50°C is complexed with tetrakis(dimethylamido)zirconium(IV) (1) to synthesize (2). The silica zirconium complex (2) is reacted with either 1-1-Bi-2-naphthol (3) or diethyl-L-tartrate (4) to produce a silica gel zirconium chiral complex (5)(6). Silica gel has different numbers of surface hydroxide groups that are sensitive to temperature, making the drying process an important process. Our results show that when silica gel is dried at a specific temperatures in an oil bath under an inert atmosphere, Zr(N(CH₃)₂)₄ (1) loses amido ligands proportional to the temp. as confirmed by solid state ¹³C and ²⁹Si NMR. The solid state NMR spectrum of silica gel supported binol zirconium(IV) (5) shows results consistent with this process. While the NMR spectrum of the silica gel supported tartrate zirconium(IV) (6) is unsymmetrical. Our current work focuses on the effectiveness of 5 as a catalyst for the [4+2] cycloaddition, and the temperature dependence of silica gel coordination modes.

Introduction

In recent years, the use of Lewis acid transition metal catalysts for asymmetric induction in [4+2] cycloaddition reactions has grown significantly for many reasons. The ability to control up to four chiral sites through C-C bond formation is a highly desirable attribute for this type of [4+2] cycloaddition. Solid supported heterogeneous catalysts have shown better recoverability, simpler processing, greater thermal and mechanical stability than homogeneous catalysts. The number of hydroxy groups found on the silica gel support available for μ-oxo bonding with Zr(N(CH₃)₂)₄ is highly dependent on the temperature at which the silica gel was dried. A surface bound zirconium complex may coordinate a chiral ligand and lead to enantiospecific catalysis by blocking multiple quadrants of approach. The presence of the different sites on the silica gel may provide other binding sites for the coordinated dienophile.

Here we report the preparation and characterization of silica gel supported zirconium binol through solid state ¹³C and ²⁹Si NMR. analyzed.

Diels-alder reaction



Results

²⁹Si CP/MAS NMR

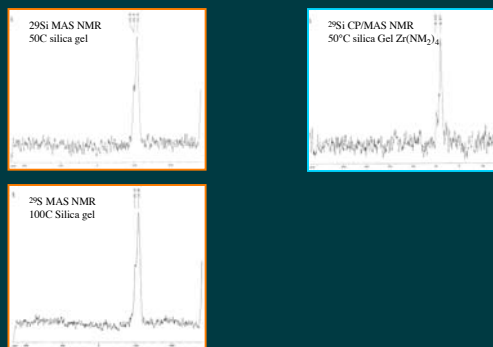
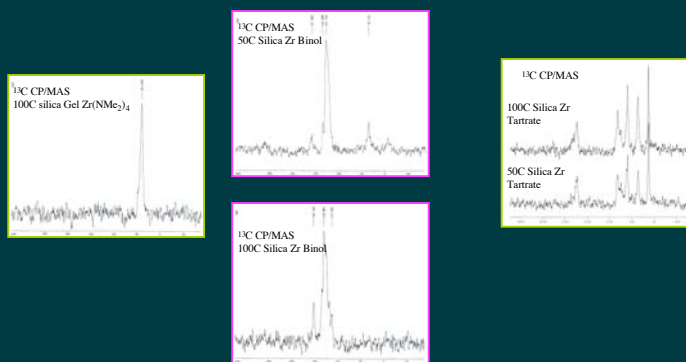


Fig. 1 ²⁹Si MAS NMR Silica gel

¹³C CP/MAS NMR



Discussion

The ²⁹Si MAS NMR spectrum of amorphous silica gel dried at 50°C shows three peaks at 100, 102, and 110 ppm, while that dried at 100°C displays only two peaks at 101 and 110 ppm. This trend is seen throughout the rest of the spectra where the 50°C samples display significantly more peaks. It is possible that interactions with silicon and oxygen atoms on local surfaces are causing anisotropic effects. The variation of binding between the zirconium-ligands and the oxygen atoms of the silica gel is another explanation for these extra peaks. The ¹³C CP/MAS NMR spectrum of 5 (50°C drying) shows a peak at 34 ppm, suggesting that not enough of the amido groups have been displaced by the alcohol groups found on the silica gel. Yet that peak is absent for 5 with 100°C drying, implying that all the amido ligands have been displaced. Both samples have peaks around 128 and 152 ppm, which are attributed to the binol's aromatic region, and the naphthoxide carbon. Although the samples of 6 were done under the same conditions as samples of 5, the ¹³C CP/MAS NMR show significantly different results, especially in the amido region. The amido peak is still apparent in both 100 °C and 50 °C of 6 proving that the amido ligands have not been completely displaced. The greater acidity of binol may be partially responsible for its apparent higher reactivity.

Conclusion

Silica gel supported 4 was successfully synthesized and characterized by solid state ¹³C and ²⁹Si CP/MAS NMR. Current work on this project focuses on replacing all amido ligands in the zirconium complex to make (O₃Si-O)₂-Zr binol 4. Compound 4 has been tested in the [4+2] cycloaddition of methyl acrylate and cyclopentadiene at room temperature and has not shown conclusive results. Future work will focus on the manipulation of chiral complexes that catalyze the [4+2] cycloaddition to produce a single enantiomer product.