

Salen Catalysts Supported on Site-Isolated Aminosilicas Prepared with Variable-sized Spacing Groups

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Introduction

Salen catalysts, represented generally in Figure 1 (A), have attracted a great deal of attention in recent decades and have been prepared with a variety of metal centers, including Co, Al, Cr, and Mn to name a few. The interest in these compounds is due to their versatility in effectively catalyzing many types of reactions such as epoxidation of alkenes, hydrolytic kinetic resolution of epoxides, selective reduction of ketones, and hetero Diels-Alder cyclizations, as well as the asymmetric induction they provide to generate a high degree of enantiomeric control [1,2]. Because of their tremendous success as homogeneous catalysts, many researchers have examined tethering modified salen catalysts onto soluble polymers or insoluble silica or polymeric materials in an effort to retain their catalytic properties while generating an easily recyclable heterogeneous catalyst [1,2].

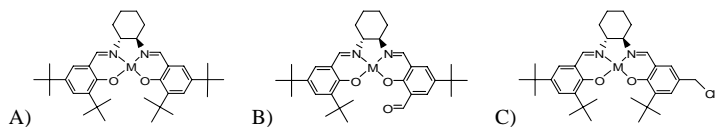


Figure 1. A) General representation of a salen catalyst. B) and C) Modified ligands for reaction with primary amines on a silica surface.

Previous research in our group has focused on creating aminosilica materials with single types of amine sites that have been shown to have different degrees of separation from one another on an SBA-15 surface (Fig. 2) [3,4]. To further understand the effects of the tethering process, we synthesized completely assembled salen catalysts from ligands B & C (Fig. 1) which could be reacted with these surfaces to probe the effects on activities imparted by the different aminosilica starting materials. We then used this information to design optimized tethering conditions for reactions proceeding via different mechanisms. The catalysts grafted on the trityl spaced aminosilicas should show less metal-metal interactions, favoring catalytic mechanisms requiring a single metal center, whereas the catalysts on benzyl spaced materials should favor mechanisms requiring two metal centers due to higher catalyst loading and closer proximity.

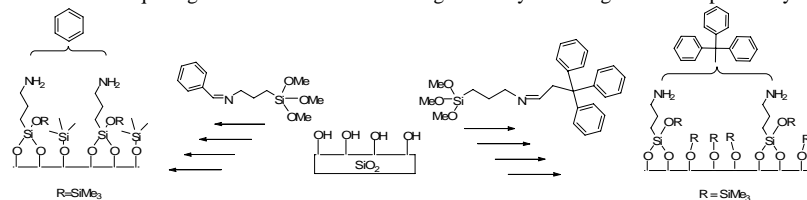


Figure 2. Schematic of the preparation of site-isolated aminosilicas.

Materials and Methods

Aminosilica materials were prepared using reported literature methods by reacting protected or unprotected aminopropyltrimethoxysilanes with SBA-15. Protected amines were converted to primary amines by hydrolysis of the protecting group [3,4]. The asymmetrical modified salen ligands were prepared from the corresponding aldehydes and enantiopure cyclohexanediamine similar to the procedure of Zheng, et al. [5]. After metalation, the salen complexes were reacted with the aminosilicas by heating at reflux conditions in toluene, and a Dean-Stark trap was used to remove residual water for ligand B (Fig. 1). The ligands, metal salen complexes, and tethered materials were characterized using solution ^1H and ^{13}C NMR, elemental analysis, mass spectroscopy, FT-Raman spectroscopy, N_2 physisorption and thermogravimetric analysis.

Results and Discussion

We have successfully synthesized ligands B and C for use in our studies. Table 1, shown below, gives a representative sample of the tethered salen complexes using ligand B. Here, we show that we do in fact have the salen complex on the aminosilica surface. For the trityl spaced aminosilica, almost all of the amine sites show cobalt loading. However, in the case of the densely functionalized material, we see that not all sites are accessible for catalyst loading, although the absolute loading is still higher than that of the trityl spaced aminosilicas. The tethered materials retain the identifying peaks of the salen functionality in the FT-Raman spectra. These materials are currently being tested in the asymmetric borohydride reduction of ketones, the hydrolytic kinetic resolution of epoxides (HKR), and Diels-Alder cyclizations as well as other reactions. We anticipate that the asymmetric reduction and Diels-Alder reactions will prefer the trityl spaced materials with either ligand, and the HKR will prefer the densely functionalized or benzyl spaced materials with the more flexible ligand C.

Table 1. Cobalt Salen Loading on Representative Aminosilicas

Material	Amine Loading	Cobalt Loading	% Coverage
Cobalt (III) Salen (ligand B) on Trityl Spaced Aminosilica	0.45 mmol $\text{NH}_2/\text{g SiO}_2$	0.43 mmol Co/g SiO_2	> 95%
Cobalt (III) Salen (ligand B) on Densely Functionalized Aminosilica	2.02 mmol $\text{NH}_2/\text{g SiO}_2$	0.73 mmol Co/g SiO_2	36%

Significance

This study furthers the understanding of how tethered catalysts are affected by surface phenomena, and it potentially provides a method to test for mono-metallic vs. bi-metallic reaction mechanisms.

References

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