

Mn(III) based binaphthyl cSchiff base complex heterogenized over organo-modified SBA-15

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Abstract

Heterogenized organocatalyst was synthesized by the covalent anchoring of the complex Schiff base manganese(III) over modified mesoporous surface of SBA-15 through the reactive 3-aminopropyl trimethoxysilane (3-APTMS) group. The XRD and N_2 sorption measurement, UV reflectance and CP MAS NMR spectroscopy (^{13}C and ^{29}Si) of the catalyst confirmed the structural integrity of the mesoporous hosts and the spectroscopic characterization technique proved the successful anchoring of the metal complex over the modified mesoporous support. The screening of the catalyst Mn(III)-L-SBA-15 and neat Mn(III)-L complexes were done in the oxidation reaction of thioanisole (methyl phenyl sulfide) by using TBHP as an oxidant. Mn(III)-L-SBA-15 catalyst shows higher activities and exhibit enhanced enantiomeric excess comparable to homogeneous catalyst [Mn(III)-L].

Keywords: Chiral Schiff-base, Binaphthyl ligand, Immobilization, Post grafting synthesis.

1. Introduction

The discovery of efficient method for catalytic epoxidation is an important goal in synthetic chemistry as there is a growing interest in using epoxide as a building block in organic synthesis^[1]. Mn(III) Schiff-base complexes have become highly valuable catalysts in homogeneous alkene epoxidation reactions by using readily available oxygen donors. In separation science SBA-15 has become the most popular member of the group possessed extremely high surface areas, easily accessible, uniform pore sizes and stability. Herein we described the covalent bonding of the Schiff base (homogeneous system) complex on modified SBA-15 surface. The immediate goal of our study was to evaluate the heterogenization method of the salen binaphthyl Schiff base ligand over SBA-15 and to determine the extent of the increased stability of the catalyst with regard to the homogeneous catalyst as well as their recycling properties.

2. Materials and Methods

The synthesis of mesoporous SBA-15 was carried out hydrothermally under the autogeneous pressure in an autoclave. Surface modification of SBA-15 was achieved by a post synthesis grafting method with 3-aminopropyl trimethoxysilane. The unsymmetrical Schiff base was prepared by the reported procedure. The surface modified SBA-15 was added to a solution of the unsymmetrical Schiff base in dry toluene and the resulting suspension was refluxed for 48 h under inert atmosphere (Fig. 1).

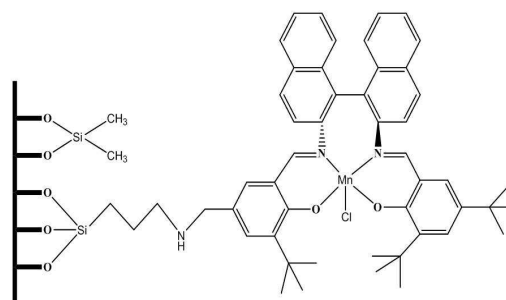


Fig. 1 Mn(III)-L-SBA-15

3. Results and Discussion

The synthesized catalysts were analyzed by a series of characterization techniques. The presence of (110) reflection^[2] in the XRD pattern confirms the retention of hexagonal ordering of SBA-15 even after functionalization and metal complex anchoring. The resulting materials were subjected to different characterization techniques, such as XRD, FT-IR, TGA-DTA, solid state ^{13}C NMR and XPS, which reveal that the metal complexes are firmly attached to modified SBA-15 support. In heterogeneous catalyst Mn(III)-L-SBA-15 XPS spectra^[3] showing two clear band at 641.7 eV and at 652.6 eV, which corresponds to Mn(III)2p_{3/2} and Mn(III)2p_{1/2} binding energy of the Mn metal respectively; where as in homogeneous neat catalyst [Mn(III)-L] XPS spectra showing two resolved peak at 642 eV and 653.1 eV. This indicates the oxidation state of Mn ion is +3 in both of the catalysts (Fig. 2). The effect of Neat Mn(III)-L complex loading on the physical properties of SBA-15

(surface area and pore size parameter) was explored by nitrogen sorption [4].

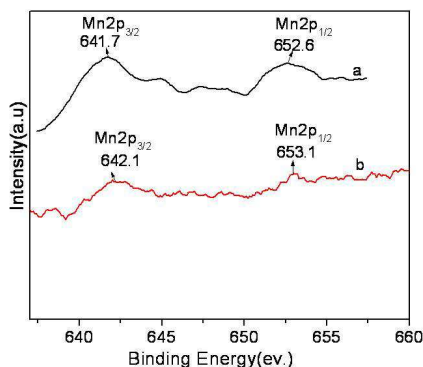


Fig. 2 XPS spectra of (a) Mn(III)-L-SBA-15, (b) Neat Mn(III)-L complex.

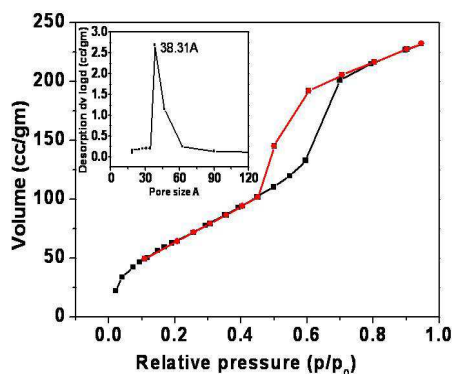


Fig. 3 Nitrogen adsorption-desorption isotherm and Pore size distribution of (inset) Mn(III)-L-SBA-15

According to IUPAC classification, type IV isotherms relate to capillary condensation steps, characteristic of the mesoporous materials. It is well known that the introduction of homogenous catalysts or metals on porous supports shows a decrease in its specific surface area and pore volume. After metal complex functionalization, the surface area gets reduced to 232 m²/gm and pore volume 0.437 cc/gm for Mn(III)-L-SBA-15. The decrease in total mesoporous pore volume (20.55%) and surface area (34.88%) after metal immobilization is indicative of the grafting of complex inside the channels of mesoporous calcined SBA-15 (Fig.3). Thus the progressive change with different modification on type IV isotherms confirms that the immobilization of Mn(III)-L complex causes pore narrowing, which resulted in a decrease in the mesoporosity of SBA-15.

The present synthesized and characterized materials Neat Mn(III)-L complex and Mn(III)-LSBA-15 were

applied for the liquid phase sulfoxidation of methyl phenyl sulfide with TBHP as an oxidant at room temperature (25°C). Immobilized Mn(III)-L-SBA-15 shows enhanced catalytic activity with 94% conversion of thioanisole along with 95% selectivity of sulfoxide (main product) in 5 hrs. Finally Mn(III)-L-SBA-15 gave high activity, TON and selectivity compared to homogeneous counterpart Mn(III)-L complex.

Further recyclability test was done up to 4th cycle and result shows almost similar conversion and selectivity from 2nd to 4th cycles (~71 % conversion at the end of 4th cycle). The observed reactivity and data are supporting the heterogeneity of the synthesized catalyst Mn(III)-L-SBA-15. The ICP analysis of the filtrate after a catalytic reaction shows the loss of Mn element from the heterogeneous catalyst Mn(III)-L-SBA-15 is less than 2% compared with the total amount of the Mn(III)-L complex grafted over the modified surface of the SBA-15.

4. Conclusions

In conclusion covalent functionalization of Mn(III)-L complex over modified surface of SBA-15 was successfully achieved by multiple synthetic procedures. The presence of (110) reflection in the XRD pattern confirms the retention of hexagonal ordering even after functionalization and metal complex anchoring. The effect of Neat Mn(III)-L complex loading on the physical properties of SBA-15 (surface area and pore parameter) was explored by nitrogen sorption. The resulting materials were subjected to different characterization techniques, which reveal that the metal complexes are firmly attached to modified SBA-15 support. The screening of the catalyst Mn(III)-L-SBA-15 was done in sulfoxidation reaction of thioanisole. Results reveal catalyst Mn(III)-L-SBA-15 shows high activity and selectivity compared to homogeneous Mn(III)-L complex counterpart. During recycling conversion of thioanisole decreases from 94 to 71% after use from fresh to fourth recycle over Mn(III)-L-SBA-15.

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