Journal of
Nanoscience and Nanotechnology
Vol. 13, 3079–3086, 2013

Chirally Functionalized SBA-15 as Efficient Heterogeneous Catalyst for Asymmetric Ketone Reduction

Umesh Balakrishnan and Sivan Velmathi*

Organic and Polymer Synthesis Laboratory, Department of Chemistry, National Institute of Technology, Tiruchirappalli 620015, Tamilnadu, India

Chiral amine catalyst was synthesized using (1R, 2S)-(-)-norephedrine and 5-chlorosalicylaldehyde by reductive amination. The structure of the catalyst was confirmed using ^{1}H-NMR and ^{13}C-NMR spectroscopic method. The catalyst was immobilized onto SBA-15 via covalent bonding using 3-chloropropyltrimethoxysilane as a reactive surface modifier under reflux condition using toluene as a solvent. The supported chiral catalyst was characterized using various physico-chemical techniques like XRD, SEM, N_2 adsorption isotherm, FTIR and UV-DRS to study the morphology, pore dimension, functional group analysis and catalyst loading in the mesoporous material. The immobilized catalyst was studied for prochiral ketone reduction using 30 mol% of chiral catalyst and boranedimethylsulphide as a stoichiometric reductant in toluene under inert atmosphere for 30 minutes. Secondary alcohols were formed up to 79% enantiomeric excess for selective ketones. Catalyst was recycled from the reaction mixture and used for further reaction without much effect on the catalytic conversion.

Keywords: Mesoporous Materials, Oxazaborolidine, SBA-15, Prochiral Ketone Reduction, Asymmetric Synthesis.

RESEARCH ARTICLE

1. INTRODUCTION

For economic, environmental and social reasons, the trend towards the catalytic application of optically pure compounds is undoubtedly increasing. Among the various methods to selectively produce single enantiomer, asymmetric catalysis is the most attractive method from the atom economic point of view.[1,2] A number of homogeneous chiral catalysts have gained wide acceptance in terms of efficiency and selectivity, and some of them are even used on an industrial scale.[3–5] One of the major drawbacks of the homogeneous catalyst is the separation of the expensive chiral catalyst from the reaction mixture at the end of the process. An obvious solution to this separation problem is the use of heterogeneous catalysts, which can be recovered from the reaction mixture by filtration or centrifugation and reused.[6] Therefore, a growing demand for the synthesis of optically active compounds in drug manufacturing has triggered a dramatic increase in fundamental research into heterogeneous chiral catalysis.

In addition to the separation advantage, the catalytic properties (selectivity and stability) of the supported catalysts are sometimes enhanced compared to the homogeneous once, which is ascribed to the contribution of the site isolation and confinement effect[7] etc. Binding of a ligand to the solid support via the covalent bond has become the most often employed method of heterogenising the chiral catalyst. The rates of the reaction for the heterogeneous catalysts were lower than the rates of the homogeneous catalysts, which is unsurprising by considering the increase in the barrier for diffusion which immobilization will always bring.

In recent years, researchers have focused on the immobilization of a chiral ligand by anchoring it onto a polymer support.[8] Polystyrene resin and silica gel have been largely used as an insoluble solid support for chiral catalysts.[9] There are some reports for the polymer bound β-amino alcohols,[10] polymer supported boron bound oxazaborolidine and polymer enlarged oxazaborolidine in membrane reactors[11] for the prochiral ketone reduction and achieved e.e upto 95% with three times recyclability of the catalyst without much loss in selectivity. However these types of polymer supports have poor textural parameters, which in turn could not able to accommodate more chiral catalyst and also the tuning of particle morphology and pore properties are difficult in this case.

*Author to whom correspondence should be addressed.

In recent years, there were lot of reports on chiral catalysis using mesoporus materials, which is mainly due to its uniform morphology and stability.[12–16] Discovery of silica based mesoporous materials like MCM-41, SBA-15 have attracted the attention of many researchers since the development of these types of molecular sieves contributed to extending the range from microporous and ordered zeolitic materials into the mesoporous regime. SBA-15 is one of a series of mesoporous materials developed in the mid-late 1990's by Stucky et al. at the University of California at Santa Barbara.[17] It has a hexagonal pore network like MCM-41, with accessible pore diameters in the range of 6–20 nm, thicker pore walls, larger pores, and higher hydrothermal stability. A typical pore size for SBA-15 is 8 nm. Both 2D and 3d mesoporous materials was used and got very high e.e. Recently, Zhang et al. published 3d flower like mesoporous architecture for asymmetric synthesis.[18] Several salen complexes immobilized on mesoporous materials for epoxidation was reported with high yield and enantioselctivity.[19] Whang et al. reported the MCM supported chiral amino alcohol for enantio selective ketone reduction.[20]

A survey of the literature reveals that compounds with three coordination sites around a boron atom will give high e.e due to their rigid structure that result in excellent enantioselectivity rather than the one with two coordination sites.[21] Tridendate chiral ligands with O, N, O hetero atoms can afford a suitable and stable coordination site for boron. The present ligand system has been designed such that it should have three donor atoms preferably O, N, O type and should behave as a tridendate ligand upon coordination with boron. In the case of O, N, O type ligands, amino alcohols play an important role.[22]

A few studies concerning the immobilization of amino alcohol derivatives onto mesoporous materials and their catalytic properties in the asymmetric reduction of ketones have been published in the open literature.[23–25] It is proposed that the confinement in chiral synthesis is essentially a consequence of elusive change in transition states induced by the weak interaction in the pores or on surface.

In our previous study, we reported the catalytic reduction of prochiral ketones using the chiral amine **1** synthesised from (1S, 2R)-(+)-norephedrine and 5-chloro salicylaldehyde under homogeneous conditions with an excellent enantiomeric excess and yield.[26]

The optimisation of reaction conditions was done for the reduction of acetophenone with ligand **1.** The enantioselectivity of ketone reduction may be affected by reaction conditions such as solvent, temperature and catalyst loading. In order to find the optimised reaction conditions for the enantioselective ketone reduction which gives high yield and enantioselectivity, the reaction was carried out at various temperatures, in various solvents and with various amount of catalyst.

Thus the optimised reaction conditions were found as 20 mol% of the catalyst, reaction time of 2 hours 30 min and refluxing temperature of THF gave the highest yield and e.e of 99% and 92% respectively. With stoichiometric amount of the catalyst also, there is no further increase in e.e and yield. In order to explore the synthetic utility of the chiral ligand **1**, enantioselective reduction of variety of prochiral ketones substituted with various substituents was studied with the optimised reaction conditions.

Our goal of developing an optimal catalyst using the chiral amine **1**, with the good potential for industrial use resulted in the decision to bind the chiral catalyst inside mesoporous materials and study its catalytic activity in the reduction of ketones using oxazaborolidine method. Mesoporous materials can be synthesized with various pore diameter which offers huge surface area and uniform pore size distribution draws the attention of researchers to use it as a support for various catalytic applications. The product (R)-1-phenyl ethanol was formed with moderate e.e of 79% with 90% yield, and also the catalyst showed some stability under the reaction conditions, hence the sensibility of the catalyst was checked upon the reuse of the catalyst, which invariably gave a small reduction in e.e and conversion. However, the loss in activity was not considered to be due to leaching of the catalyst from the surface.

2. EXPERIMENTAL DETAILS

2.1. Materials Methods

Experiments were performed under nitrogen atmosphere. Solvents were distilled from the appropriate drying agents prior to use. All the chemicals were purchased from Aldrich and Merck and used without further purification. Enantiomeric excess was measured using a Shimadzu 10A HPLC instrument and chiralcel OD-H chiral column. BET surface area and pore size measurements were recorded in Micromeritics Gemini V-2380 model. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions were obtained from the adsorption branch of the nitrogen isotherms by Barrett–Joyner–Halenda method. Specific rotations were recorded using Rudolph Autopol IV digital polarimeter. UV-DRS spectra were recorded in Shimadzu spectrometer Model 160. Thermal measurements of the samples were carried out on a Mettler Toledo instrument. Microanalysis of the material was done on a Carbo Erba Analyser model 1106. FTIR spectra were recorded using Perkin Elmer spectrum one spectrometer. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using Cu Kα ($\lambda = 0.154$ nm) radiation. The diffractograms were recorded in the 2θ range of 0.8 to 10° with a 2θ step size of 0.01° and a step time of 10 seconds. Scanning electron microscopy analysis of the sample was done with a JEOL-JSM 6300 model instrument.

2.2. Synthesis of Chiral Amine 1 from 5-Chloro Salicylaldehdye and (1R, 2S)-(-)-Norephedrine

Chiral amine **1** was synthesized based on the method reported by us earlier.[26] Melting point: 52–54 °C. $[\alpha]_{35}^{589} = +11.1$ ($c = 0.2$, $CHCl_3$). FTIR (cm^{-1}): 3630 (–OH), 3340 (–NH), 3098 (ar–CH), 1238 (C–O). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.01$ (*d*, 3 H), 2.9 (*q*, 1 H), 3.15 (*s*, 1 H), 4.0 (dd, 2 H), 4.8 (*d*, 1 H), 6.7–7.4 (Ar–H, 8 H) ppm. ^{13}C NMR, $CDCl_3$, δ ppm: 14, 49, 57, 75, 117.8, 123.5, 124.2, 126.2, 127.8, 127.9, 128.4, 128.5, 141.2, 157. 220. Elemental Anal. Calcd: C, 65.86; H, 6.22; N, 4.8. Found: C, 64.38; H, 6.63; N, 4.79.

2.3. Synthesis of SBA-15

Highly ordered mesoporous SBA-15 support was synthesized by the procedure previously reported by Zhao et al.[27] under hydrothermal conditions using a triblock organic copolymer as a template. In a typical synthesis, triblock copolymer (4 g), poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO_{20}–PO_{70}–EO_{20}) (Pluronic P123, MW 5800) was dispersed in double-distilled water (40 g) followed by the addition of 2 M aqueous HCl (120 ml) under stirring at ambient temperature (35 °C) for 3 h. Finally, tetraethyl orthosilicate (4 g) was added to the homogeneous solution under stirring to form a gel at 40 °C for 24 h. The resultant gel was allowed to stand for crystallization under static hydrothermal condition at 100 °C for 48 h in a Teflon Parr reactor. The white colored solid product was filtered off, washed with warm distilled water several times, and dried at 100 °C overnight. The as-synthesized solid product was calcined at 540 °C in air for 24 h to remove the organic template. The calcined material was characterized using low angle powder XRD, BET isotherm and SEM technique.

2.4. Synthesis of 2-((1-hydroxy-1-phenylpropan-2-ylamino)methyl)-5-(3-(trimethoxysilyl) propyl)Phenol(2)

Coupling of the chiral amine 1 with 3-Cl propyl trimethoxysilane and immobilising on SBA-15 was done similar to the procedure reported elsewhere.[28–30] ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.75$ (*t*, $^3J = 4.5$ Hz, 2 H, Si–CH_2–), 1.17 (*d*, $^3J = 6.5$ Hz, 3 H, CH–CH_3), 1.21 (*q*, $^3J = 4.3$ Hz, 2 H, CH_2–CH_2–CH_2), 1.9 (*t*, $^3J = 4.1$ Hz, 2 H, CH_2–CH_2–), 2.05 (*s*, 1 H, CHNH), 2.5 (*b*, *s*, 1 H, CH–OH), 3.4 (sep, $^3J = 7.5$ Hz, 1 H, CH–CH_3), 3.8 (*dd*, $^3J = 2$ Hz, 2 H, CH_2–NH), 4.3 (*d*, 2.1 Hz, 1 H, CH–OH), 5.3 (*s*, 9 H, OCH_3), 5.4 (*s*, 1 H, Ph–OH), 6.9 (*d*, 1 H, Phenyl H), 7.0 (*d*, 1 H, phenyl H), 7.1 (*d*, 1 H, phenyl H), 7.24–7.34 (*m*, 5 H, Ar–H) ppm. $[\alpha]_{35}^{589} = +25.3$ ($c = 0.1$ in methanol).

2.5. Immobilization of Modified Chiral Amine Ligand on SBA-15 (3)

Calcined SBA-15 (1 g) was added to the toluene solution of above synthesized 2 and the suspension was allowed to stir at reflux temperature under nitrogen atmosphere for 48 h. After cooling, the powder was collected by filtration, washed successively with dry toluene, and then dried under vacuum. Dried material was subjected to soxhlet-extraction with dichloromethane for 24 h. Finally the sample was dried under vacuum at 45–50 °C. IR (KBr) cm^{-1}: 3340, 2950, 2857, 1635, 1439, 1251, 964, 807, 796 and 558.

2.6. Synthesis of Trimethylsilyl Capped Chiral Ligand Immobilized SBA-15 (4)

Under extremely dry condition, a suspension of above synthesized 3 (1 g) and hexamethyl disiloxane (HMDS) (0.1 ml) was refluxed overnight with stirring under nitrogen atmosphere. The solvent was removed under reduced pressure in a rotary evaporator and the dry powder was washed two or three times with dry ethanol (10 ml) by centrifugation and finally dried under vacuum at 80 °C for 8 h. Material recovery was $\geq 98\%$. TMS capping of chiral amine immobilized SBA-15 was confirmed by IR spectroscopy.

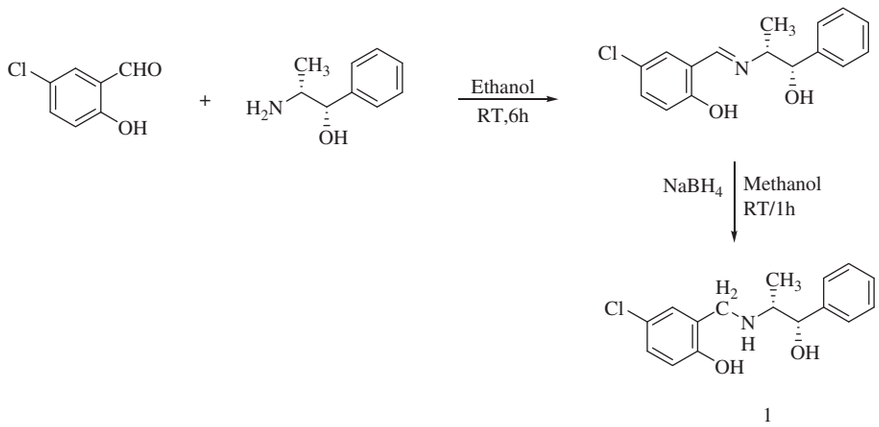
2.7. Asymmetric Borane Reductin of Prochiral Ketone Using SBA-15 Immobilized Catalyst (4)

The chiral amine ligand **1** immobilized SBA-15 (**4**) (320 mg, 30 mol%) was dissolved in dry toluene. Borane dimethyl sulfide (BMS) (0.03, 0.3 mmol) was added drop wise and then the reaction mixture was refluxed for half an hour followed by the drop wise addition of acetophenone (0.025, 0.1 mmol). The reaction mixture was continuously refluxed for 12 hours, cooled to room temperature, and filtered. To the filtrate, 2 N HCl was added and extracted with dichloromethane. (R)-1-phenyl ethanol was separated by column chromatography with silica gel as an adsorbent and 98:2 hexane:ethyl acetate as an eluant.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Immobilised Chiral Ligand

Chiral amine ligand **1** was synthesized by the condensation of 5-chloro salicylaldehyde and (1R, 2S)-(-)-norephedrine. The imine formed was reduced to the corresponding amine using $NaBH_4$/Methanol (Scheme 1). This chiral catalyst 1 was reported by us for asymmetric ketone reduction[26] and asymmetric carbon–carbon addition[31] under homogeneous (in solution phase) conditions with very good enantiomeric excess and yield. On seeing the merits of the catalyst, we focused our attention to immobilize this β-amino alcohol



Scheme 1. Synthesis of chiral catalyst 1.

derived chiral amine onto mesoporous materials in order to make this catalyst for marketing potential.

Mesoporous materials usually have high surface area and uniform pore size distribution with a wide range of crystalline arrangement. By modifying the reaction conditions like the temperature, pH, concentration of tetraethylorthosilicate (silica source), we can tune the pore diameter which is useful to load the catalyst of any diameter without affecting the optical geometry of the catalyst which is also the essential parameter for the selectivity.

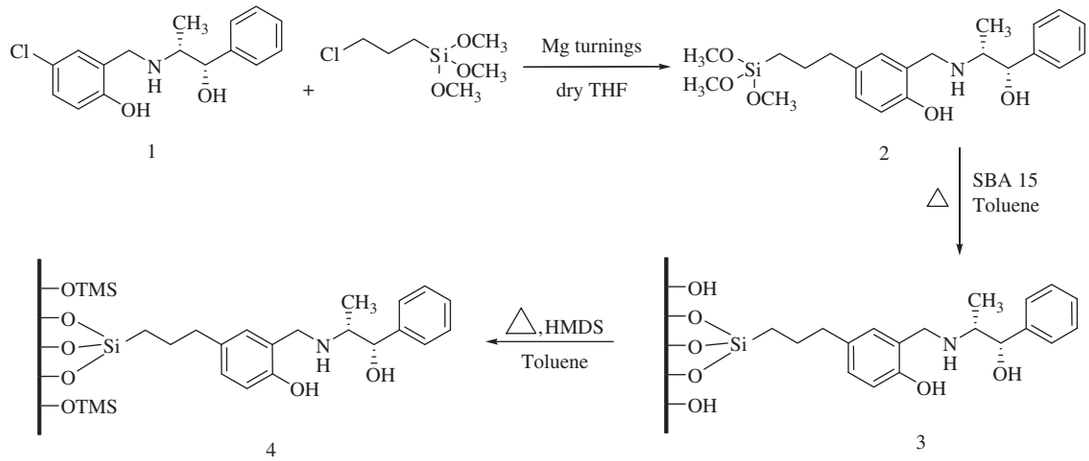
To start with, we immobilised the catalyst **1** in SBA-15 (Scheme 2) through covalent grafting method. After the encapsulation, the catalyst was washed several times with different solvents, until no more chiral ligand was detected in the supernatant of the washing solvents. Earlier there are reports mentioning that the unreacted silanol groups affect the catalytic reaction especially for oxazaborolidine mediated ketone reductions.[30] Thus, it is essential to cap the unreacted silanol groups with tri methyl silyl (TMS) groups after the immobilisation of the chiral catalyst. The chiral amine ligand immobilised on SBA-15 was treated with HMDS to cap the free silanol groups.

3.2. Characterization of the SBA-15 Anchored Chiral Ligand

The catalyst present inside the pores can be confirmed by various physico-chemical techniques like FTIR, UV-DRS, Powder-XRD, N_2-adsorption desorption and SEM, EDAX etc. The amount of ligand present inside the pores can be confirmed from TGA and CHN elemental analysis techniques. From the weight percentage of nitrogen we determined the catalyst present inside the material, which was found to be 0.02 mmol% per 100 mg of the catalyst. Also TGA which showed a weight loss around 180 °C indicates the presence of nitrogen and further loss in weight around 550–590 °C due to the loss of carbon and hydrogen.

3.3. XRD Studies

XRD patterns for the pure SBA-15 and the chiral catalyst immobilised SBA-15 (4) are shown in Figure 1. It shows a well resolved (100) reflection and several higher order reflections at 2θ angles between 1.5 and 3° indicating



Scheme 2. Synthesis of a heterogenised chiral ligand using SBA-15.

RESEARCH ARTICLE

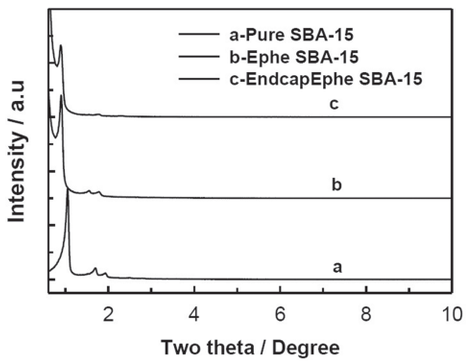


Fig. 1. Powder XRD pattern of pure SBA-15, Ephe-immobilized SBA-15 and end capped Ephe-immobilized SBA-15.

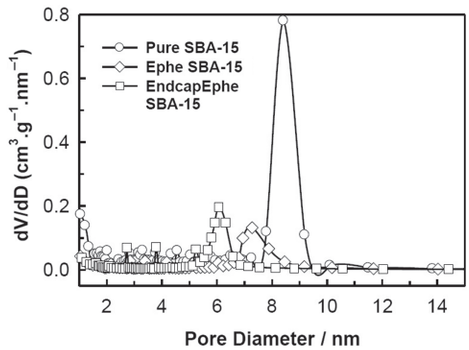


Fig. 3. BJH pore size distribution of pure SBA-15, Ephe-immobilized SBA-15 and end capped Ephe-immobilized SBA-15.

excellent structural ordering with the symmetry of *P6mm* space group for both the samples. The XRD patterns are almost similar to that of the previously reported SBA-15 material. This indicates that all the materials even after the modification with chiral amine ligands, exhibit well ordered two-dimensional hexagonal structure with linear arrays of pores which are arranged in regular intervals. It is interesting to note that the intensity of the peaks at lower angle for the catalyst immobilised SBA-15 is much lower than that of the parent SBA-15. The reduction in the intensity of the peaks is mainly due to the encapsulation of the chiral amine inside the mesochannels.

3.4. N_2 Sorption Studies

Figure 2 shows the nitrogen adsorption isotherm of SBA-15 and ligand anchored SBA-15 (4) which shows a perfect type IV isotherm corresponding to mesoporous material with surface area of 486.1 m^2/g and pore size of around 8 nm. Though after immobilisation, surface area decreases dramatically up to 122.7 m^2/g because some of the active sites at the surface were replaced by the chiral catalyst. It has also been found that the capillary condensation step of the isotherms of ligand anchored SBA-15 is shifted towards lower relative pressure, indicating that

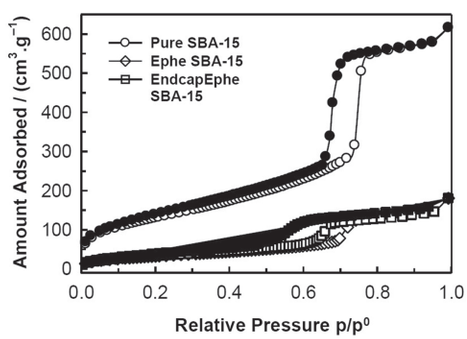


Fig. 2. Nitrogen adsorption–desorption isotherms of pure SBA-15, Ephe-immobilized SBA-15 and end capped Ephe-immobilized SBA-15

the pore size of the support is also decreased after modification, which is evident from Figure 3. The decrease in surface area, pore volume and the pore diameter of the modified sample ensures the presence of chiral amine ligand molecules inside the mesochannels.

As expected, the modification of the SBA-15 support with the chiral amine has caused a significant change in the textural parameters of the support. The amount of nitrogen adsorbed decreases for the immobilised SBA-15 shows the surface area and pore volume are lower than pure SBA-15. Table I shows the surface area, pore volume and the pore diameter data for all the mesoporous materials taken for this study.

3.5. FTIR, UV Studies and SEM Studies

Figure 4 shows the FTIR spectrum of SBA-15, ligand immobilized SBA-15 and end capped SBA-15, which clearly reveals the anchoring of the chiral amine ligand inside the mesoporous channels of SBA-15. The peak corresponding to the vibrational modes of SBA-15 are 3328 cm^{-1} for OH and around 1076 cm^{-1} for Si—O—Si bond and sharp peak at 945 cm^{-1} for Si–OH were present in the case of pure SBA-15 and also in the ligand immobilized SBA-15. There are also peaks observed in the range of 3100–2900 cm^{-1} and 1200–800 cm^{-1} confirming the presence of the chiral catalyst inside the channels. Also the intensity of OH vibration decreases in the case of end capped SBA-15 which indicates that the free silanol groups were capped by TMS group. However, most of the peaks related to the pure chiral ligand were not observed for the chiral ligand anchored SBA-15. This confirms that pure

Table I. Textural parameters of pure and chiral ligand immobilized SBA-15 mesoporous molecular sieves during various synthetic steps.

S. no.	Sample name	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore diameter (nm)
1	SBA-15	486.1	0.889	8.41
2	CL-SBA-15	122.2	0.234	7.27
3	Endcapped	129.8	0.224	6.06

RESEARCH ARTICLE

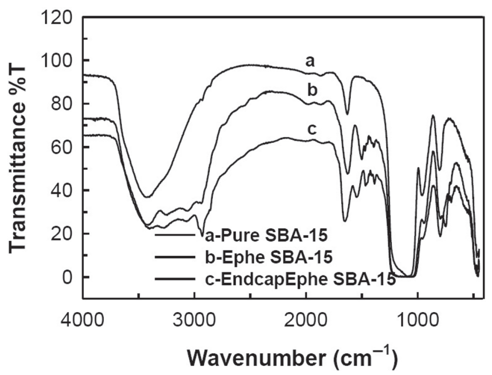


Fig. 4. FT IR spectrum of pure SBA-15, Ephe-immobilized SBA-15 and end capped Ephe-immobilized SBA-15.

chiral catalyst is anchored well inside the pores and not simply physisorbed at the external surface.

The stability of the chiral amine ligand inside the meso channels of SBA-15 was investigated by UV-DRS spectroscopy. Figure 5 shows the UV-DRS spectrum of pure SBA-15 and the chiral ligand immobilised SBA-15. Pure chiral ligand 1 exhibits two sharp bands in the UV spectrum, which are centred at 253 and 338 nm corresponding to the π–π^* and n–π^* transitions. In the case of chiral ligand modified SBA-15, the intensity of these bands is much lower than that of the pure chiral amine ligand 1. This is mainly due to the low concentration of the ligand in the mesochannels of SBA-15. Also there was slight shift in absorption frequency, which can be attributed to the inducement interaction between NH group and the catalyst. The arrangement of the chiral ligands in the well-ordered mesopore channels of the SBA-15 support, confirms that the ligands are perfectly immobilized inside the mesochannels and are highly stable even after the immobilization.

The morphology of the SBA-15 before and after the chiral ligand modification was analysed by HRSEM. Figures 6(a) and (b) show the HRSEM images of the SBA-15 support before the chiral amine ligand 1 encapsulation taken at low and high resolution, respectively. Figures 6(c) and (d) show the images of the SBA-15 after ligand immobilization at low and high magnification. As can be seen

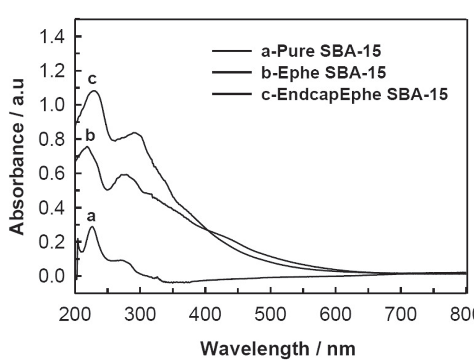


Fig. 5. UV-DRS spectrum of pure SBA-15, Ephe-immobilized SBA-15 and end capped Ephe-immobilized SBA-15.

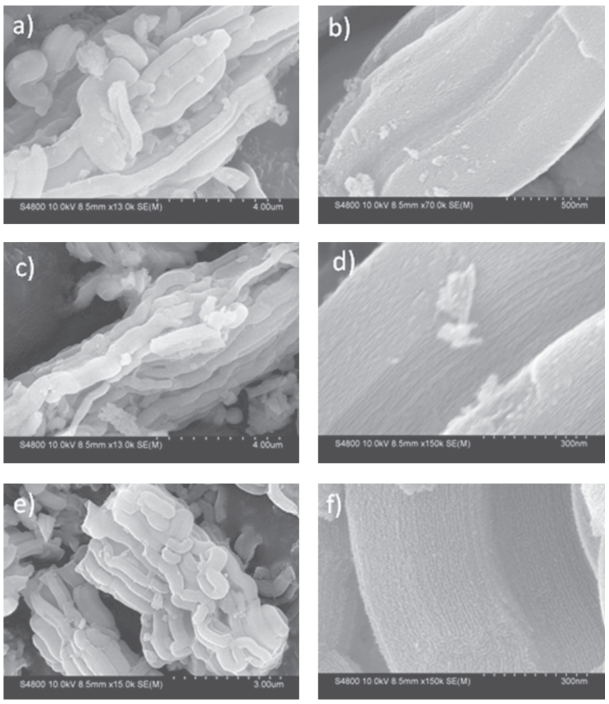


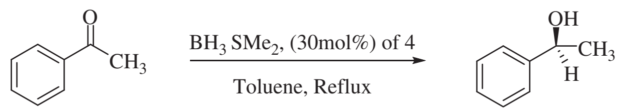
Fig. 6. HRSEM image of (a) and (b) pure SBA-15, (c) and (d) Ephe-immobilized SBA-15 and (e) and (f) end capped Ephe-immobilized SBA-15 in low and high resolution respectively.

from the figures, both the samples exhibit rod like particles as in the case of SBA-15 and are uniform in size and shape. Similar morphology was observed in the case of SBA-15 end capped with TMS also (Figs. 6(d) and (e)). The encapsulation of chiral catalyst onto the mesopores was confirmed from EDAX elemental mapping analysis. It is important to note that the structure and the morphology of the materials are not affected even after the modification with the chiral amine ligand 1 in SBA-15. The retention of structural morphology after immobilisation was also in good agreement with the XRD and nitrogen adsorption data. From all these results, it can be concluded that the SBA-15 is more stable due to its thick walls, and is an excellent support for the immobilization of different functionalities inside the mesochannels due to its two dimensional arrangement.

3.6. Enantioselective Ketone Reduction Using SBA-15 Anchored Catalyst 4

We studied the prochiral ketone reduction using the SBA-15 immobilised chiral catalyst 4 using borane dimethylsulphide through the formation of oxazaborolidine complex and *N*-coordinated borane as a stoichiometric reductant (Scheme 3). The mechanism for the asymmetric ketone reduction was already discussed in our previous paper.[17] The product (R)-1-Phenyl ethanol was formed up to 70% ee with over 90% chemical yield which was determined through chiral HPLC using Chiralcel OD-H column. Under homogenous condition the reaction was

RESEARCH ARTICLE



Scheme 3. Reduction of acetophenone with the chiral ligand encapsulated SBA-15.

carried out with the 20 mol% of the catalyst. However, in the present study, we used 30 mol% of the heterogeneous catalyst for the reaction and it was filtered from the reaction mixture towards the end of the catalytic reaction. Then the heterogeneous catalyst was washed thrice with dichloromethane and dried in vacuum oven at 60 °C for 6 h.

We also did the recyclable study using the filtered catalyst, there was a marginal decrease in the enantiomeric excess of the product 1-phenyl ethanol to 66% e.e in the second trial and 59% in the third trial. This is due to the silanol groups in SBA-15 which were not completely capped by hexamethyl disiloxane, which can form a complex with borane dimethyl sulphide either at the surface or at the pores. This may also be due to the oxazaborolidine complex which was not completely removed by adding methanol while filtering the chiral catalyst. Then repeated washing with DCM could not ensure the complete removal of the catalyst. Only by adding dil. HCl, we can achieve the complete removal of the complex at the surface, but this may results in leaching of the chiral catalyst which affects the porosity of the mesopores. We also checked the activity of the catalyst 4 by employing the reduction reaction for different prochiral ketones and got the e.e upto 79%. The results are presented in Table II. Ketones with electron withdrawing group (entry 4, 5, 6 and 9) were reduced with high e.e than the ketones with electron releasing group (entry 7 and 8).

Generally, chiral catalyst will get anchored both in the surface as well as inside the channels. The steric interaction between the substrate and surface and also the diffusion properties of the substrates inside that small channels results in low e.e. Since SBA-15 gave high e.e the catalytic reaction for the other aliphatic ketones and further studies are underway to optimise the results and to improve the recycle studies with SBA-15 which will be published in due course.

Table II. Reduction of aromatic ketones with the chiral amine ligand encapsulated SBA-15.[a]

S. no.	Ketone	Yield (%)[b]	e.e (%)[c]	Absolute configuration[d]
1	Acetophenone	92	70	R
2	SBA-15-1st trial	87	66	R
3	SBA-15 2nd trial	75	59	R
4	*p*-Cl acetophenone	79	79	R
5	*p*-Br-acetophenone	81	70 (99)	R
6	*p*-I-acetophenone	85	55	R
7	*p*-CH_3 acetophenone	56	15 (40)	R
8	*p*-OCH_3 acetophenone	67	23 (99.8)	R
9	*m*-NO_2-acetophenone	71	45	R

Notes: [a]Reaction were carried out in dry toluene at 105 °C for 12 h using 30 mol% of catalyst; [b]Isolated yield by column chromatography; [c]The enantiomeric excess was determined by HPLC analysis using chiralcel OD-H column. Values in parentheses indicate the e.e obtained under homogeneous condition; [d]The absolute configuration was determined by the sign of optical rotation using digital polarimeter.

4. CONCLUSIONS

The ordered mesoporous materials have been synthesised and chiral β-amino alcohol derived catalyst was immobilised onto these porous materials in order to develop a novel heterogenised catalyst. These catalysts were employed in the asymmetric ketone reduction through oxazaborolidine formation at higher temperature. SBA-15 supported catalyst gave better enantioselectivity upto 79% e.e and 92% yield. The enantioselectivity largely depends on the surface properties like optical geometry, pore diameter and the number of silanol groups.

Acknowledgment: The authors thank Dr. S. Sundararajan, Director, NITT for encouragement and support and DST for the financial support in the form of a major sponsored project (SR/S1/OC-142-2011).

References and Notes

1. E. N. Jacobsen, A. Pfaltz, and H. Yamamoto, Comprehensive Asymmetric Catalysis I–I II, Springer-Verlag, Berlin **(1999)**.
2. I. Ojima, Catalytic Asymmetric Synthesis, Wiley-VCH, New York **(2000)**.
3. R. Noyori and M. Kitamura, *Angew. Chem. Int. Ed.* 30, 49 **(1999)**.
4. E. J. Corey, and C. J. Helal, *Angew. Chem. Int. Ed.* 37, 1986 **(1988)**.
5. H. C. Brown, Y. M. Choi, and S. Narasimhan, *J. Org. Chem.* 47, 3153 **(1982)**.
6. C. E. Song, J. S. Lim, S. C. Kim, K. J. Lee, and D. Y. Chi, *Chem. Commun.* 24, 2415 **(2000)**.
7. C. Li, *Catal. Rev.* 46, 419 **(2004)**.
8. Q. H. Fan, Y. M. Li, and A. S. C. Chan, *Chem. Rev.* 102, 3385 **(2002)**.
9. Y. M. Chen and H. K. Rhee, *Catal. Lett.* 82, 249 **(2002)**.
10. C. Franot, G. B. Stone, P. Engrli, C. Spondlin, and E. A. Waldvogel, *Tetrahedron: Asymmetry* 6, 2755 **(1995)**.
11. G. Giffels, J. Beliczey, M. Felder, and U. Kragl, *Tetrahedron: Asymmetry* 9, 691 **(1998)**.
12. K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji, and J. P. Hill, *Bull. Chem. Soc. Jpn.* 85, 1 **(2012)**.
13. N. Suzuki, S. Kiba, and Y. Yamauchi, *J. Nanosci. Nanotechnol.* 12, 983 **(2012)**.
14. Y. Chen, X. Shi, B. Han, H. Qin, Z. Li, Y. Lu, J. Wang, and Y. Kong, *J. Nanosci. Nanotechnol.* 12, 7239 **(2012)**.
15. P. Yang, S. Gai, and J. Lin, *Chem. Soc. Rev.* 41, 3679 **(2012)**.
16. P. A. Monson, *Microporous Mesoporous Mater.* 160, 47 **(2012)**.
17. D. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science* 279, 548 **(1998)**.
18. L. Zhang, Y. Guo, J. Peng, X. Liu, P. Yuan, H. Q. Yang, and C. Li, *Chem. Commun.* 47, 4087 **(2011)**.
19. R. B. Kawthekar, Y. Lee, and G. J. Kim, *J. Porous Mater.* 16, 367 **(2009)**.

RESEARCH ARTICLE

20. W. M. Sun, K. Y. Kwon, and G. J. Kim, *J. Ind. Eng. Chem. Res.* 8, 262 **(2002)**.
21. Z. X. Shen, J. Lu, Q. Zhang, and Y. W. Zhang, *Tetrahedron: Asymmetry* 8, 2287 **(1997)**.
22. L. N. Huang, X. P. Hui, and P. F. Xu, *J. Mol. Catal. A: Chem.* 258, 216 **(2006)**.
23. N. Bellocq, D. Brunel, M. Lasperas, and P. Moreau, *Stud. Surf. Sci. Catal.* 108, 485 **(1997)**.
24. M. Lasperas, N. Bellocq, D. Brunel, and P. Moreau, *Tetrahedron: Asymmetry* 9, 3053 **(1998)**.
25. D. S. Shephard, W. Zhou, T. Maschmeyer, J. M. Matters, C. L. Roper, S. Parsons, B. F. G. Johnson, and M. J. Duer, *J. Angew. Chem. Int. Ed.* 37, 2719 **(1998)**.
26. U. Balakrishnan, N. Ananthi, and S. Velmathi, *Tetrahedron: Asymmetry* 20, 1150 **(2009)**.
27. Y. Shi, R. Liu, B. Tu, and D. Zhao, *J. Am. Chem. Soc.* 129, 9522 **(2007)**.
28. A. P. Bhatt, K. Pathak, R. V. Jasra, R. I. Kureshy, N. H. Khan, and S. H. R. Abdi, *J. Mol. Catal. A: Chem.* 244, 110 **(2006)**.
29. K. Pathak, A. P. Bhatt, S. H. R. Abdi, R. I. Kureshy, N. H. Khan, I. Ahmad, and R. V. Jasra, *Tetrahedron: Asymmetry* 17, 1506 **(2006)**.
30. K. Li, Z. Zhou, L. Wang, Q. Chen, G. Zhao, and Q. Z. C. Tang, *Tetrahedron: Asymmetry* 14, 95 **(2003)**.
31. R. W. Parrott and S. R. Hitchcock, *Tetrahedron: Asymmetry* 19, 19 **(2008)**.

Received: 30 October 2012. Accepted: 28 December 2012.