

Chiral lanthanum–lithium–binaphthol complex covalently bonded to silica and MCM-41 for enantioselective nitroaldol (Henry) reaction

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Abstract

A chiral BINOL ligand covalently anchored on silica and mesoporous MCM-41 was synthesized and characterized by powder XRD, FT-IR, N₂ adsorption–desorption measurements, TGA and elemental analysis. These anchored ligands were then used to prepare La–Li–BINOL–silica **1a** and La–Li–BINOL–MCM-41 **1b** complexes. The immobilized catalysts having lanthanum content around 0.12–0.18 mmol/g were tested as enantioselective catalyst for Henry reaction and ee 55–84% were found which were comparable to its homogeneous counterpart. The solid catalysts can be reused by simple filtration and recycled several times without much loss in performance.

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1. Introduction

Chirally pure binaphthol (BINOL) has found its application in the synthesis of enantioselective catalysts for diverse reactions under homogeneous conditions [1–10]. Immobilization of such a versatile ligand to prepare a heterogeneous catalyst is pertinent from environmental and economical points of view. Heterogeneous catalysts offer several advantages such as simplification of post-reaction work-up, easy separation from the reaction mixture, reuse and the possibility to design continuous flow processes [11–14]. Previous reports on heterogenization of BINOL largely dealt with its anchoring on organic polymers [15–21]. However, organic polymers have drawbacks as they swell/shrink depending on the solvent that result into diffusional problems and difficulty in their reuse. Therefore, we have attempted to anchor chiral BINOL ligand on a robust inorganic support such as amorphous silica and mesoporous MCM-41. MCM-41 in particular offers several advantages: (a) MCM-41 is an ordered array of hexagonal channels with a 25–40 Å pore diameter, which offers uniform catalyst structure with lower diffusional resistance to the substrate molecules for their easy

access to the catalytically active sites located within the channels, (b) it is rugged porous material that retain the exposed framework in a wide range of reaction media and do not shrink or swell in different solvents and (c) it has a considerably large surface area and therefore reasonably high catalyst loading with minimum diffusional resistance can be achieved that would help to overcome the activity decrease generally observed in heterogenization of the homogeneous catalysis due to inefficient interfacial mass transfer between the liquid phase and the solid. On the other hand, amorphous silica is (a) chemically inert with high thermal stability, (b) easily available for large-scale applications and (c) is microporous where catalyst loading is largely on surface, thereby minimal diffusional constraints. We, therefore, modified chiral BINOL by introducing silanol arm at its sixth position and anchored it on high surface silica and MCM-41. These solid ligands were then used to prepare La–Li–BINOL–silica (**1a**) and La–Li–BINOL–MCM-41 (**1b**) complexes that were studied as a catalyst in a representative enantioselective nitroaldol (Henry) reaction [22].

The nitroaldol (Henry) reaction is one of the most important reactions for direct carbon–carbon bond formation [23–26] where the product β-hydroxy-nitroalkanes can be transformed into valuable building blocks [27,28], e.g., to amines by reduction [29], to carbonyl compounds by the Nef reaction [30] and to nitroalkenes by dehydration [31–33]. The cat-

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alytic enantioselective version of Henry reaction was first reported, using heterobimetallic lanthanide BINOL catalyst systems under homogeneous condition. Herein, we report heterogeneous version of asymmetric nitroaldol (Henry) reaction using **1a** and **b** as catalysts. To the best of our knowledge, a lanthanum–lithium–BINOL chiral complex covalently linked to inorganic support has not been reported.

2. Experimental

(*R*)-2,2'-Dihydroxy-1,1'-binaphthalene (BINOL), lanthanum chloride heptahydrate and aldehydes were purchased from Aldrich and were used as such. Cetyltrimethylammonium bromide, amorphous silica (SiO₂, 350 mesh) (s.d. Fine Chem. Ltd., India) and sodium silicate solution (27.34% SiO₂ and 8.05% Na₂O) (Kadvani Chemicals, India) were of commercial grade. All the solvents were of analytical quality and were dried by standard methods before use.

¹H and ¹³C NMR spectra were recorded on 200 MHz NMR spectrometer (Bruker, F113V). The IR spectra were recorded on Perkin-Elmer Spectrum GX spectrophotometer in KBr/nujol mull. Electronic spectra were recorded in dichloromethane on Hewlett-Packard Diode Array spectrophotometer Model, 8452A. Microanalysis of the complex was done on CHNS analyser, Perkin-Elmer model 2400. Inductive coupled plasma spectrometer (Perkin-Elmer, USA, model ICP Optima 3300 RL) was used for La estimation. Estimation of bromine was done by gravimetric analysis. Powder X-ray diffraction patterns of the samples were recorded with Philips X'pert MPD diffractometer using Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation with 2θ step size of 0.02° and step time of 5 s of curved Cu K α monochromator under identical conditions. Thermal measurement of the samples were carried out on a Mettler Toledo (TGA/SDTA 851^e) instrument. A 10 mg of sample was heated from room temperature to 700°C at a heating rate of $10^\circ\text{C min}^{-1}$ in flowing N₂.

BET surface area was determined using N₂ sorption data measured at 77 K using volumetric adsorption set-up (Micromeritics ASAP-2010, USA). The pore diameter of the samples was determined from the desorption branch of the N₂ adsorption isotherm employing the Barret–Joyner–Halenda (BJH) model [34]. The ee of nitroalcohols was determined by HPLC (Shimadzu SCL-10AVP) using Chiralcel columns (AD, OD, OD-H).

2.1. Synthesis of (*R*)-6-bromo-2,2'-dihydroxy-1,1'-bi-naphthalene **3**

The compound (*R*)-6-bromo-2,2'-dihydroxy-1,1'-binaphthalene **3** was synthesized from BINOL **2** according to the reported procedure [17].

2.2. Synthesis of (*R*)-6-bromo-2,2'-dimethoxy-1,1'-bi-naphthalene **4**

To a well-stirred solution of (*R*)-6-bromo-binaphthol **3** (5 g, 13.69 mmol) in anhydrous acetone (160 ml) were added anhydrous K₂CO₃ (5.67 g, 41.13 mmol) and methyl iodide (5.83 g, 41.13 mmol) and the mixture was heated at reflux under dry con-

dition for 18 h. After cooling, the volatiles were removed under vacuum and the residual solid was dissolved in CH₂Cl₂ (175 ml) and H₂O (150 ml). The aqueous layer was further extracted with CH₂Cl₂ (3 \times 60 ml). The combined organic layer was dried over anhydrous Na₂SO₄. The solvent was removed and the pale yellow product was washed with methanol and subjected to flash column chromatography (hexane/dichloromethane, 3/2) to get **4** as white solid (4.6 g, 87%). IR (KBr) 3064, 3048, 2958, 2933, 2904, 2836, 1616, 1587, 1505, 1493, 1461, 1343, 1320, 1265, 1251, 1133, 1064, 1019, 963, 895, 807, 749, 779, 706, 672, 592 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 3.75 (s, 6H), 6.94 (d, $J = 9.2 \text{ Hz}$, 1H), 7.11 (d, $J = 9.2 \text{ Hz}$, 1H), 7.18–7.27 (m, 3H), 7.47 (d, $J = 9 \text{ Hz}$, 2H), 7.84 (d, $J = 6.6 \text{ Hz}$, 1H), 7.89 (d, $J = 5.7 \text{ Hz}$, 1H), 7.95 (d, $J = 10.8 \text{ Hz}$, 1H), 8.01 (d, $J = 2.8 \text{ Hz}$, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 57.3, 110.1, 111.3, 117.1, 118.2, 123.8, 124.0, 125.7, 127.1, 128.3, 129.5, 129.8, 130.2, 130.6, 130.8, 131.3, 132.3, 152.1, 152.7. Anal. Calcd. C₂₂H₁₇BrO₂: C, 67.19; H, 4.36; Br, 20.32. Found: C, 67.02; H, 4.47; Br, 20.13.

2.3. Synthesis of MCM-41

A highly ordered hexagonal siliceous MCM-41 was synthesized according to the procedure described in Ref. [35]. The sodium silicate (27.34% SiO₂ and 8.05% Na₂O) was used as a silica source and cetyltrimethylammonium bromide (CTAB) as a template. Precursor gel of composition 1SiO₂:0.33Na₂O:0.5CTAB:74H₂O was used for the synthesis of MCM-41.

2.4. Synthesis of (*R*)-6-(1-propyltrimethoxy silane)-2,2'-dimethoxy-1,1'-bi-naphthalene **7**

A 250-ml, three-necked, round-bottomed flask was provided with a mechanical stirrer, an addition funnel with a guard tube containing fused CaCl₂, a thermometer and a reflux condenser, the top of which was connected with a bubbler and an argon line by way of a three-way stopcock. All parts of the apparatus were thoroughly dried. The flask was flushed with argon and charged with 0.2 g magnesium turnings, 15 ml of dry, degassed THF and a crystal of iodine. To the resultant mixture, (*R*)-6-bromo-2,2'-dimethoxy-1,1'-bi-naphthalene (0.5 g, 1.27 mmol) in 15 ml dry, degassed THF was added drop wise over a period of 30 min. The mixture was stirred at room temperature until the color of iodine faded. The flask was gently warmed to initiate the reaction and if necessary a crystal of iodine was further added. The mixture was allowed to stir at 65°C for 9 h and then cooled to room temperature. To the above resulting mass, a solution of 3-chloropropyltrimethoxy silane **6** (0.24 ml, 1.32 mmol, in 10 ml of dry THF) was added dropwise over a period of 40 min. The reaction mixture was further stirred at 65°C for 12 h and the solvent was removed under vacuum. Dry toluene (75 ml) was added to the residue that was further stirred for 2 h and filtered under inert atmosphere to afford **7** in solution. The compound **7** is highly moisture sensitive hence an aliquot from the above solution was taken for spectroscopic characterization, while rest of the solution was directly used for the preparation of **8a** and **b**. ¹H NMR (200 MHz, CDCl₃) δ 0.92 (broad t, $J = 7$, 2H), 0.75–0.85

(m, 2H), 1.84 (broad t, $J=7$ Hz, 2H), 3.56 (s, 9H), 3.75 (s, 6H), 6.95 (d, $J=9$ Hz, 1H), 7.02 (d, $J=9$ Hz, 1H), 7.17–7.35 (m, 3H), 7.42 (d, $J=3.8$ Hz, 1H), 7.48 (d, $J=3.5$ Hz, 1H), 7.84 (d, $J=8.5$ Hz, 1H), 7.88 (d, $J=9$ Hz, 1H), 7.95 (d, $J=9$ Hz, 1H), 8.0 (d, $J=2$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 7.4, 8.7, 26.9, 47.8, 50.9, 51.3, 114.9, 115.8, 124.0, 125.6, 125.9, 126.7, 126.8, 127.0, 127.5, 127.8, 128.5, 128.6, 129.1, 129.4, 130.0, 130.2, 130.4, 130.5, 149.9, 150.1.

2.5. General procedure for the synthesis of 2,2'-dimethoxy-1,1'-bi-naphthalene on silica/MCM-41 **8a** and **b**

Silica (freshly activated at 250 °C)/calcined MCM-41 (1.8 g) was added to the above solution containing **7** and the mixture was allowed to stir at 75 °C under argon atmosphere for 42 h. After cooling, the powder was collected by filtration, washed successively with dry THF and then dried under vacuum. Dried material was subjected to Soxhlet-extraction with dichloromethane for 10 h. Finally sample was dried under vacuum at 45–50 °C.

2.6. General procedure for the synthesis of BINOL anchored on solids **9a** and **b**

2,2'-Dimethoxy-1,1'-bi-naphthalene supported solid (2.0 g) was taken in anhydrous CH_2Cl_2 (20 ml) and cooled to –78 °C. BBr_3 (3 ml, 3.0 mmol, 1 M solution in CH_2Cl_2) was added to it dropwise with continuous stirring for 2 h. After that the reaction mixture was brought to room temperature, stirred for additional 2 h and an aqueous saturated solution of NaHCO_3 (18 ml) was slowly added to it. The resulting solid, henceforth, denoted as BINOL–MCM-41 was filtered off, washed successively with water, dry acetone, dry dichloromethane and finally dried at 55 °C under vacuum for 10 h.

2.7. General synthesis of **1a** and **b**

To a suspension of **9a** and **b** (2.28 g; 0.40 mmol ligand) in dry THF (20 ml) a solution of 1.60N *n*-butyl lithium in hexanes (0.85 ml, 1.36 mmol) was added under argon at 0 °C and the resulting mass was stirred for 4 h. The lithated compound was collected by filtration under dry and inert atmosphere, taken in dry THF (20 ml) and a solution of preformed dilithium(*R*)-binaphthoxide (0.238 g, 0.80 mmol, 2 equivalent) was added with continuous stirring at room temperature. To the above mixture was added dropwise a THF solution containing $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.148 g, 0.40 mmol, 1 equivalent) and NaO^tBu (0.23 ml, 0.12 mmol, 0.52N in THF) and the resulting mass was stirred vigorously overnight at room temperature followed by heating at 50 °C for 60 h. After cooling to room temperature, the immobilized catalysts **1a** and **b**, was filtered and washed repeatedly with THF and dichloromethane on Soxhlet extractor for 12 h in order to remove any free La–Li–BINOL complex formed during the above-mentioned process. Finally immobilized catalyst was dried under vacuum at 50 °C. Microanalysis, for **1a**, found: C, 14.92; H, 1.34. For **1b**, found: C, 10.09; H, 0.91.

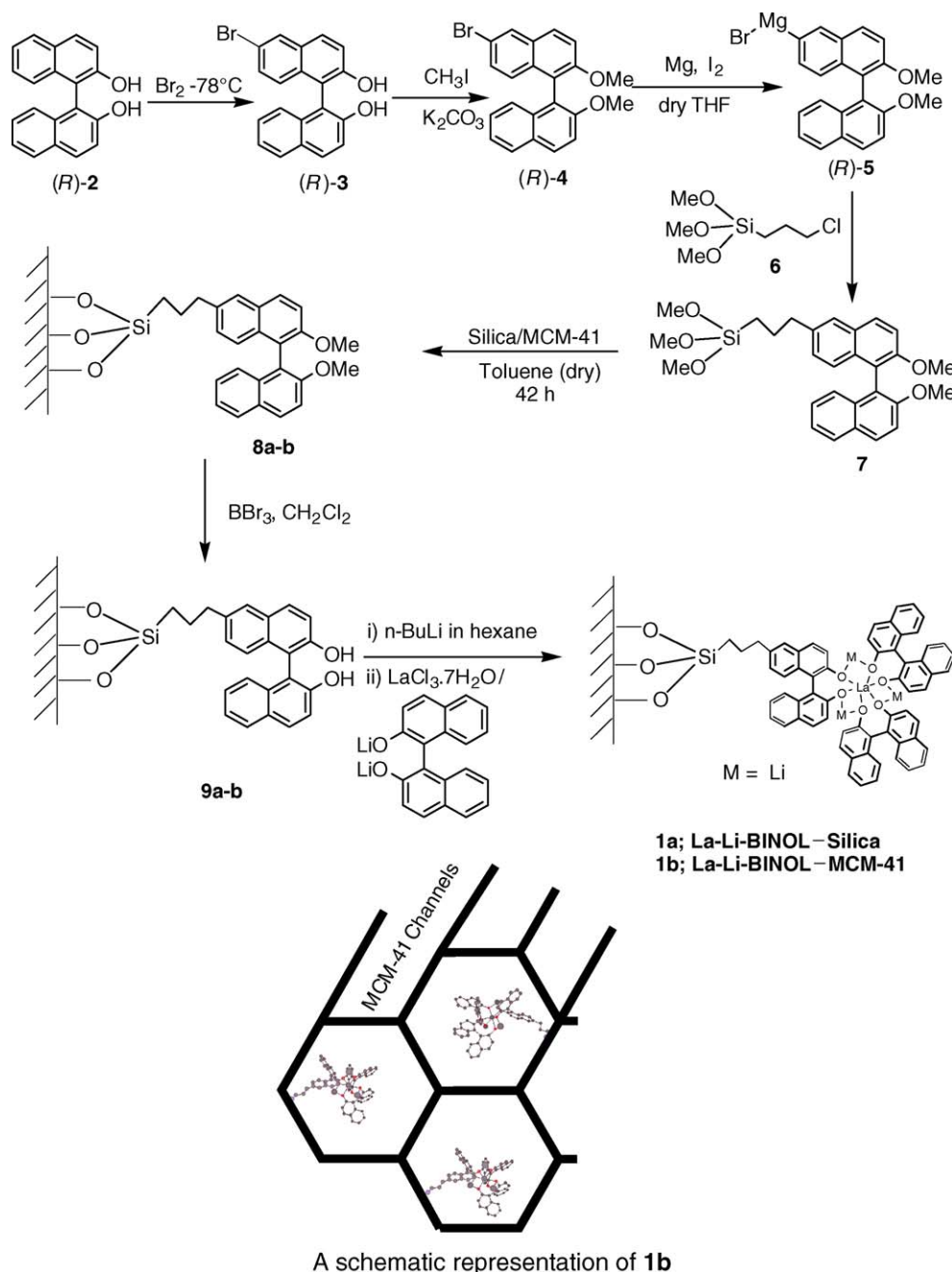
2.8. General procedure for enantioselective Henry reaction of aldehydes with nitromethane

In a dry 20-ml double-walled glass vessel, a suspension of catalyst **1a/1b** (0.045 mmol) in dry THF (6 ml) was magnetically stirred for 30 min at –42 °C. To this mixture was added nitromethane (13.6 mmol), after a gap of 40 min an appropriate aldehyde (1.36 mmol) was added drop wise and stirred for 18–42 h. The conversion was monitored on HPLC. After completion of the reaction, immobilized catalyst **1a/1b** was filtered from the reaction mixture and washed thoroughly with THF and dried under vacuum for re-use. The product was isolated and purified by flash chromatography (SiO_2 , hexane/ethyl acetate 96:4) and enantiomeric excess (ee) was determined by HPLC using chiralcel AD, OD, OD-H column (hexane:IPA, 90:10, 254 nm).

3. Results and discussion

In order to retain the flexibility of the free BINOL and to develop the catalyst system closer to the structure that was used under homogeneous condition, we synthesized catalysts **1a** and **b** according to the steps as shown in Scheme 1. Thus, (*R*)-BINOL was monobrominated at its sixth position by controlled stoichiometric addition of bromine. The mono-brominated BINOL was O-methylated with CH_3I , which was then treated with Mg/I_2 to get Grignard complex (*R*)-**5** that was reacted with 3-chloropropyltrimethoxysilane **6** to get O-methylated BINOL with a silanol arm **7**. The compound **7** was refluxed with calcined silica/MCM-41 in toluene to afford **8a** and **b**, which was demethylated to achieve (*R*)-BINOL anchored on solids **9a** and **b**. These compounds were used as solid BINOL ligand for the synthesis of lanthanum–lithium–BINOL covalently bonded to silica/MCM-41 and depicted as catalysts **1a** and **b**. The accomplishment of the covalent anchoring was assessed by analytical and spectroscopic characterization of the resulting solids.

The solid support MCM-41 itself and different stages of its surface modification, compounds **9b** and **1b** were characterized by powder X-ray diffraction. X-ray diffraction pattern for MCM-41 given in Fig. 1 shows the presence of the four reflection peaks corresponding to 1 0 0, 1 1 0, 2 0 0 and 2 1 0 typically reported for MCM-41 confirming the presence of ordered hexagonal mesoporous structure [36]. These four peaks fit a hexagonal unit cell with α_0 4.513 nm. For compound **9b** the d_{100} spacing and α_0 values are 3.889 and 4.490 nm, respectively. After the formation of catalyst **1b** inside the channels of MCM-41 these peaks are further reduced in intensity with slight shift to smaller d spacing of 3.611 nm and α_0 values is 4.169 nm (Fig. 1), but XRD patterns were essentially the same as that of the calcined MCM-41, signifying the conservation of the mesoporous texture during the immobilization process. These changes might be due to a partial loss of the space correlation of the pores were commonly observed in studies of silylation of mesoporous silicas. The intensity of the Bragg reflections originates from the difference in the scattering power between the silica walls and the empty pores. Due to the presence of the complex inside the pores, the amount of scattering power within the pores is



Scheme 1. Preparation of LLB covalently bonded to silica/mesoporous MCM-41.

increased, resulting in overall loss of intensity due to phase cancellation between pore walls and the guest complex [37]. Therefore, it can be concluded that the formation of the BINOL catalyst has taken place preferentially inside the pore system of the MCM-41.

Fig. 2 shows the FT-IR spectra of (a) calcined MCM-41; (b) BINOL anchored MCM-41 (**9b**); (c) solid catalyst **1b**. The FT-IR spectra of MCM-41 showed the characteristic band at 1079 cm^{-1} of Si–O–Si and 3431 cm^{-1} of Si–OH bond (Fig. 2a). Some characteristic peaks at 2960 and 2848 cm^{-1} for aliphatic CH_2 stretching, 1438 for CH_2 bending (Fig. 2b and c) in FT-IR spectra of **1b** suggest successful anchoring of complex on MCM-41.

Nitrogen sorption isotherms were measured at liquid N_2 temperature (77 K) using Micromeritics ASAP 2010 system (Norcross, GA, USA). Silica samples were degassed at 383 K for 6 h prior to analysis. BET surface area was calculated using adsorption data in the BET region ($P/P_0 = 0.05\text{--}0.3$) and the pore size distribution of the samples was determined from desorption branches of the isotherms by the BJH method. The pore size distribution of the samples was also determined by KJS method taking N_2 desorption reported on hydrophobic silica, RO1 (ODMS LiChrospher Si-1000), as a reference material. Total pore volume of the samples was estimated on the basis of the amount of N_2 adsorbed at relative pressure of about 0.995 . The primary mesopore volume V_p was calculated from

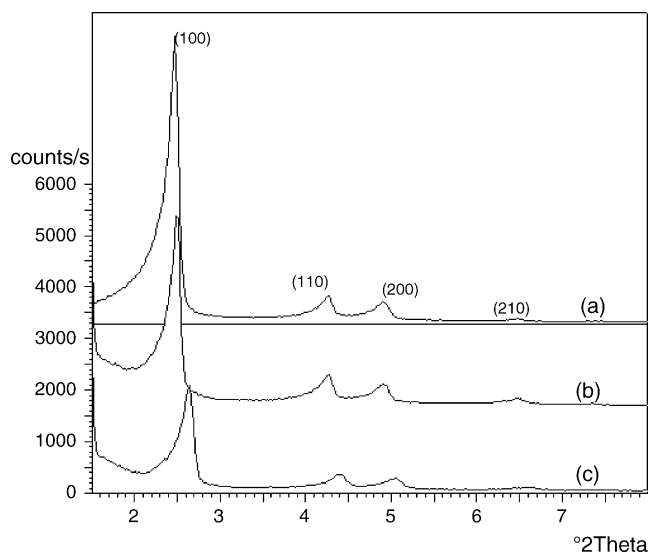


Fig. 1. XRD patterns of calcined MCM-41 (a), compounds **9b** (b) and **1b** (c).

the slope of a linear portion of the t -plot in the pressure range above the pressure of nitrogen condensation in primary mesopores. The data obtained from the N_2 adsorption measurements are summarized in Table 1. The surface area, pore volume and pore diameters of **9b** and the solid catalyst (**1b**) were as expected for mesoporous materials (Table 1). Moreover, the

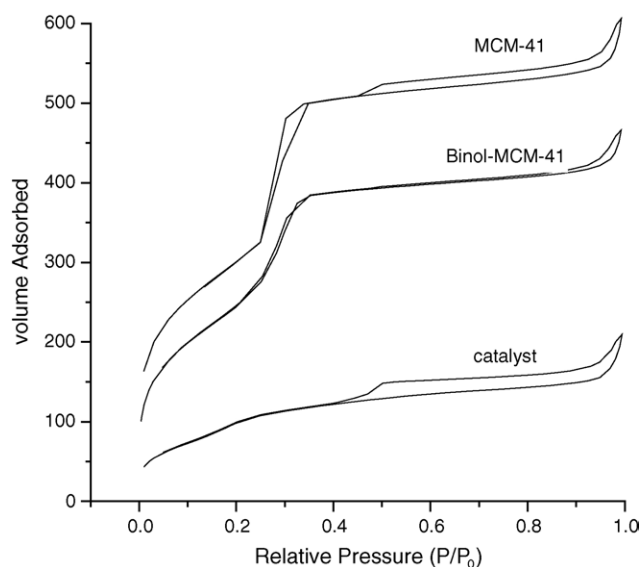


Fig. 3. Nitrogen adsorption/desorption isotherms of MCM-41, **9b** and solid catalyst (**1b**).

porosity measurements of pristine MCM-41, **9b** and **1b** reveal type IV IUPAC adsorption–desorption isotherms (Fig. 3). As presented in Table 1, the BET surface and the pore volume of the heterogeneous catalyst (**1b**) are lower as compared to pristine MCM-41. Upon immobilization, the mean pore diameter

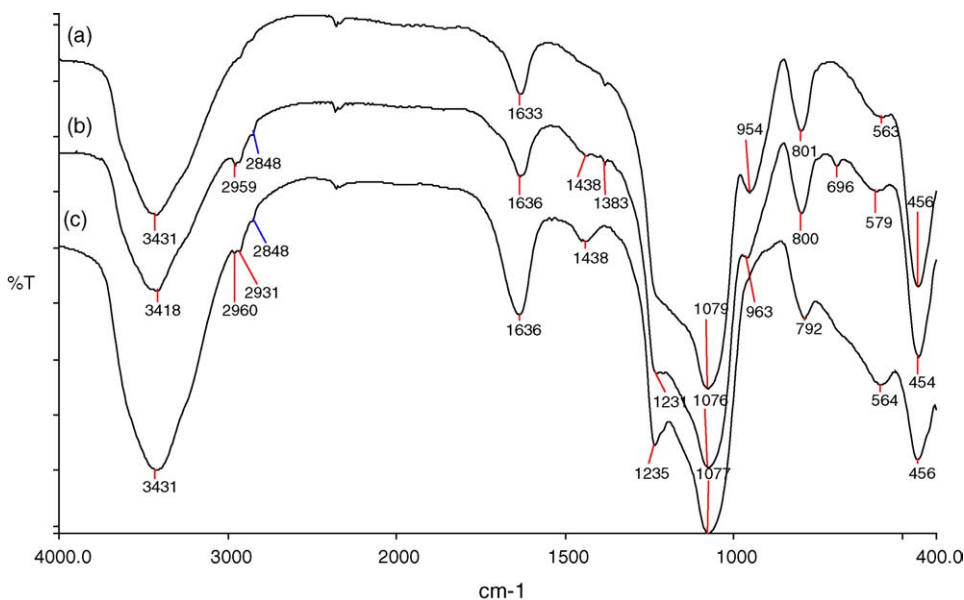


Fig. 2. The FT-IR spectra of MCM-41 (a), **9b** (b) and **1b** (c).

Table 1
Physico-chemical characterization data of MCM-41, compound **9b** and catalyst **1b**

Compound	La loading (mmol/100 mg)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	BJH pore diameter (Å)	Wall thickness (Å)
MCM-41	–	1094	0.9272	32.3	12.8
9b	–	904	0.7345	31.9	13.0
1b	0.01778	675	0.5941	28.3	13.4
Silica	–	358	–	–	–
1a	0.01193	204	–	–	–

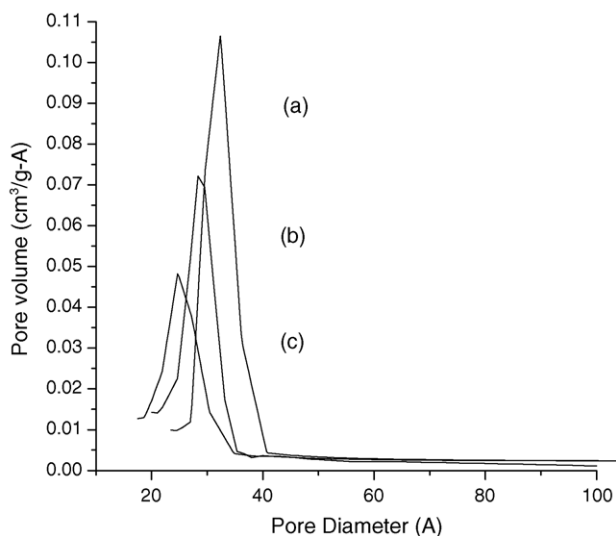


Fig. 4. BJH pore-size distributions of MCM-41 (a), **9b** (b) and **1b** (c).

(Fig. 4) also shows a decrease as indicated by the shift of the main peak to smaller values in pore size distribution with a successive strong decrease in nitrogen adsorbed. All these results indicate that the internal pores of the MCM-41 are occupied by the catalytic complex and the structure of the mesopores is maintained after modification. A pictorial representation of the lanthanum–lithium–BINOL complex covalently grafted to the channels of MCM-41 is shown in Scheme 1.

The loading of the complex **1a** was found to be 0.12 mmol/g and **1b** was 0.17 mmol/g as determined by ICP analysis. It was further confirmed by XRF and combustion chemical analysis.

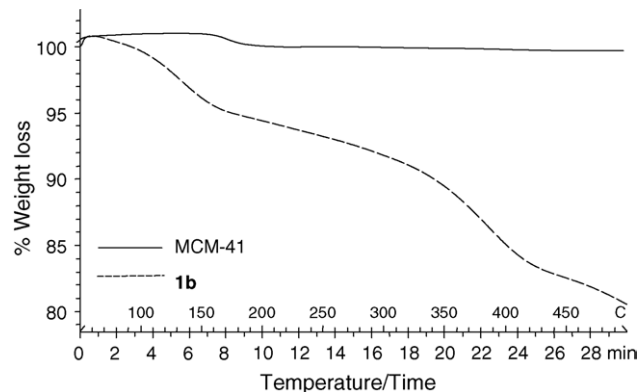


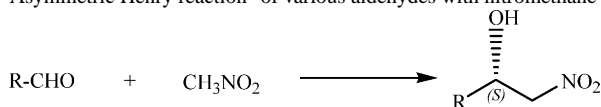
Fig. 5. TGA-curve of calcined MCM-41 and heterogeneous catalyst (**1b**).

Fig. 5 shows thermogravimetric analysis (TGA) of MCM-41 and **1b**. TGA analysis of calcined MCM-41 showed no change in weight loss on increasing the temperature after an initial weight loss of 0.3% that was observed due to the loss of moisture present inside the MCM-41 channels. However, the thermogram of the immobilized complex **1b** showed a two-step decomposition pattern due to the presence of organic ligand present in the complex. In the first step the weight loss was 3.9% between 50 and 220 °C and in the second step the weight loss was 15.7% between 220 and 500 °C.

The catalytic activity of the silica-supported catalysts **1a** and **b** was evaluated for the enantioselective nitroaldol reaction of various aldehydes with nitromethane in THF and the results are summarized in Table 2. Immobilized catalyst **1a** gave ee (55–76%) with yield (74–86%) for cyclohexancarboxaldehyde,

Table 2

Asymmetric Henry reaction^a of various aldehydes with nitromethane using immobilized catalysts **1a** and **b**



Entry	R-group	Catalyst	Time (h)	Temperature (°C)	Yield (%) ^b	ee (%) ^c
1 ^d	Cyclohexyl	LLB	18	−42	91	90
2	Cyclohexyl	1a	28	−42	86	76
3	Cyclohexyl	1b	28	−42	78	84
4 ^d		LLB	34	−42	94	62
5		1a	41	−42	87	55
6		1b	41	−42	83	57
7 ^d		LLB	18	−42	80	85
8		1a	34	−42	74	65
9		1b	34	−42	64	77
10 ^d	Ph-CH ₂ -CH ₂	LLB	21	−42	83	73
11	Ph-CH ₂ -CH ₂	1a	30	−42	78	62
12	Ph-CH ₂ -CH ₂	1b	30	−42	77	67
13 ^e	Ph-CH ₂ -CH ₂	MCM-41	30	−42	00	–

^a All reactions were performed by using catalyst (0.045 mmol), aldehyde (1.36 mmol) and nitromethane (13.6 mmol) in THF.

^b Isolated yield.

^c Enantiomeric excess determined by HPLC using Chiralcel AD, OD, OD-H columns.

^d Reaction conducted under homogeneous condition.

^e Blank reaction was carried out of by using hydrocinnamaldehyde with nitromethane in the presence of neat calcined MCM-41.

Table 3
Results of the recycling of the catalyst **1b** in the reaction of hydrocinnamaldehyde with nitromethane^a

Entry	R-group	Time (h)	Temperature (°C)	Yield (%)	ee (%)
14	Ph-CH ₂ -CH ₂ (first time)	30	-42	77	67
15	Ph-CH ₂ -CH ₂ (second time)	33	-42	76	63
16	Ph-CH ₂ -CH ₂ (third time)	38	-42	68	64
17	Ph-CH ₂ -CH ₂ (fourth time)	42	-42	66	62

^a All reactions were performed by using catalyst (0.045 mmol), aldehyde (1.36 mmol) and nitromethane (13.6 mmol).

hexanal, isobutyraldehyde and hydrocinnamaldehyde (Table 2, entries 2, 5, 8, 11), while for immobilized catalyst **1b** the ee was found in the range of 57–84% for the same aldehydes (Table 2, entries 3, 6, 9, 12). The results are comparable to its homogeneous counterpart (LLB) (Table 2, entries 1, 4, 7, 10). However, reaction took longer time with immobilized catalyst. In general, catalyst **1a** afforded better yields compared to **1b**, since in **1a** the reaction is taking place on the surface of silica while in the case of **1b** it is happening inside the channels of MCM-41 where diffusional constrain would be relatively higher. However, catalyst **1b** was found to be more enantioselective than **1a**. Nevertheless, the activity of the homogeneous catalyst LLB is still better than immobilized catalysts **1a** and **b**.

Blank experiment with calcined MCM-41 showed no catalytic activity (Table 2, yield: 0%, entry 13) towards reaction of hydrocinnamaldehyde with nitromethane. Hence, the catalytic activity is entirely attributed to the complex immobilized on MCM-41.

Recyclability of the immobilized catalysts was checked for nitroaldol reaction with hydrocinnamaldehyde as representative substrate with nitromethane. After the first catalytic run, the catalyst was separated by filtration under inert atmosphere, washed thoroughly with dichloromethane, dried and subjected to another cycle with fresh reaction mixture, under similar reaction conditions. The enantioselectivity was found nearly the same for three reuse experiments, but the reaction took longer time (Table 3, entries 14–17). In order to check the leaching of La-complex, the filtrate obtained after separation of catalyst was subjected to UV–vis and ICP analysis that showed no trace of La. Further, in separate catalytic run the filtrate was supplied with fresh quantities of the reactants such as hydrocinnamaldehyde and nitromethane, which showed no further increase in nitroaldol product by HPLC analysis after 36 h. These experiments suggest that the reactive complex is firmly intact in the MCM-41 channels and no leaching of the catalyst takes place under the nitroaldol reaction condition.

The recycled catalyst (after one cycle) was characterized by XRD spectra, FT-IR and CHN analysis, which suggested the partial degradation of the complex and the entrapment of reactant within the silica matrix that may be the reason for the gradual slow down of the reaction in the subsequent recycle experiments.

4. Conclusions

In conclusion, we have carried out the synthesis and characterization of chiral BINOL ligand anchored on silica and MCM-41. These anchored BINOL were then used to prepare

La–Li–BINOL–silica (**1a**) and La–Li–BINOL–MCM-41 (**1b**) complexes, and were characterized by different analytical and spectral techniques. These immobilized complexes have shown promising activity and selectivity in enantioselective Henry reaction. High yield with ee (55–84%) was obtained in the case of aliphatic aldehydes. The catalyst could be separated by simple filtration and reused up to three times without any significant change in enantioselectivity but with some loss in activity. Further, work towards the issue related to better ee in the product and better diffusion of reactants and product by immobilization of this complex in bigger pore size solid support is in progress and the results would be communicated in due course of time.

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References

- [1] M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1236.
- [2] L. Pu, *Chem. Rev.* 98 (1998) 2405.
- [3] E.N. Jacobsen, A. Pfaltz, H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer, New York, 1999.
- [4] I. Ojima, *Catalytic Asymmetric Synthesis*, second ed., Wiley, New York, 2000.
- [5] S. Kobayashi, H. Ishitani, *Chem. Rev.* 99 (1999) 1069.
- [6] J. Inanaga, H. Furuno, T. Hayano, *Chem. Rev.* 102 (2002) 2211.
- [7] H.C. Aspinall, *Chem. Rev.* 102 (2002) 1807.
- [8] P. Walsh, *Chem. Rev.* 103 (2003) 3297.
- [9] W. Zhang, *Chem. Rev.* 104 (2004) 2531.
- [10] K. Mikami, Y. Itoh, M. Yamanaka, *Chem. Rev.* 104 (2004) 1.
- [11] J.H. Clark, D.J. Macquarrie, *Org. Proc. Res. Dev.* 1 (1997) 149.
- [12] S. Ernst, R. Gläser, M. Selle, *Stud. Surf. Sci. Catal.* 105 (1997) 1021.
- [13] J.H. Clark, D.J. Macquarrie, *Chem. Soc. Rev.* 25 (1996) 303.
- [14] A. Heckel, D. Seebach, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 1.
- [15] H. Sellner, C. Faber, P.B. Rheiner, D. Seebach, *Chem. Eur. J.* 6 (2000) 3692.
- [16] S. Matsunaga, T. Ohshima, M. Shibasaki, *Tetrahedron Lett.* 41 (2000) 8473.
- [17] D. Jayaprakash, H. Sasai, *Tetrahedron Asymmetry* 12 (2001) 2589.
- [18] P. Hesemann, J.J.E. Moreau, C. Yixiang, *Tetrahedron Asymmetry* 13 (2002) 607.
- [19] D. Jayaprakash, Y. Kobayashi, S. Watanabe, T. Arai, H. Sasai, *Tetrahedron Asymmetry* 14 (2003) 1587.
- [20] T. Sekiguti, Y. Lizuka, S. Takizawa, D. Jayaprakash, T. Arai, H. Sasai, *Org. Lett.* 5 (2003) 2647.
- [21] X.-W. Yang, J.-H. Sheng, C.S. Da, H.-S. Wang, W. Su, R. Wang, A.S.C. Chan, *J. Org. Chem.* 65 (2000) 295.

- [22] (a) N. Ono, *The Nitro Group in Organic Synthesis*, Wiley–VCH, New York, 2001, p. 30, Chapter 3;
(b) H. Sasai, T. Suzuki, S. Arai, T. Arai, M. Shibasaki, *J. Am. Chem. Soc.* 114 (1992) 4418;
(c) M. Shibasaki, N. Yoshikawa, *Chem. Rev.* 102 (2002) 2187;
(d) C. Christensen, K. Juhl, K.A. Jørgensen, *Chem. Commun.* (2001) 2222;
(e) D.A. Evans, D. Seidel, M. Rueping, H.W. Lam, J.T. Shaw, C.W. Downey, *J. Am. Chem. Soc.* 125 (2003) 12692;
(f) B.M. Trost, V.S.C. Yeh, *Angew. Chem. Int. Ed. Engl.* 41 (2002) 861;
(g) Y. Kogami, T. Nakajima, T. Ikeno, T. Yamada, *Synthesis* (2004) 1947;
(h) J.C. Borah, S. Gogoi, J. Boruwa, B. Kalita, N.C. Barua, *Tetrahedron Lett.* 45 (2004) 3689;
(i) Y.-W. Zhong, P. Tian, G.-Q. Lin, *Tetrahedron: Asymmetry* 15 (2004) 771;
(j) S.-F. Lu, D.-M. Du, S.-W. Zhang, J. Xu, *Tetrahedron: Asymmetry* 15 (2004) 3433.
- [23] Y.M.A. Yamada, N. Yoshikawa, H. Sasai, M. Shibasaki, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1871.
- [24] B. List, R.A. Lerner, C.F. Barbas III, *J. Am. Chem. Soc.* 122 (2000) 2395.
- [25] B.M. Trost, H. Itoh, E.R. Silcoff, *J. Am. Chem. Soc.* 123 (2001) 3367.
- [26] A.B. Northrup, D.W.C. MacMillan, *J. Am. Chem. Soc.* 124 (2002) 6798.
- [27] F.A. Luzio, *Tetrahedron* 57 (2001) 915.
- [28] D. Seebach, A.K. Beck, T. Mukhopadhyay, E. Thomas, *Helv. Chim. Acta* 65 (1982) 1101.
- [29] M. Watanabe, K. Murata, T. Ikariya, *J. Org. Chem.* 67 (2002) 1712.
- [30] H. Chikasita, Y. Morita, K. Itoh, *Synth. Commun.* 17 (1987) 677.
- [31] M. Anbazhagan, G. Kumaran, M. Sasidharan, *J. Chem. Res., Synop.* 9 (1997) 336.
- [32] G. Rosini, R. Ballini, *Synthesis* (1988) 833.
- [33] H.W. Pinnick, in: L.A. Paquette (Ed.), *Organic Reactions*, vol. 38, Wiley, New York, 1990, Chapter 3.
- [34] E.P. Barrett, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.* 73 (1951) 373.
- [35] C. Pérez, S. Pérez, G.A. Fuentes, A. Corma, *J. Mol. Catal. A: Chem.* 197 (2003) 275.
- [36] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [37] F.J. Brieler, P. Grundmann, M. Fröba, L. Chen, P.J. Klar, W. Heimbrot, H.-A. Krug von Nidda, T. Kurz, A. Loidl, *J. Am. Chem. Soc.* 126 (2004) 797.