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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, N_2 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.

Keywords: Asymmetric catalysis; Heterogeneous catalysis; Enantioselective Henry reaction; BINOL–MCM-41; MCM-41 as support; Silica as support

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 constrains. 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 (SiO_2, 350 mesh) (s.d. Fine Chem. Ltd., India) and sodium silicate solution (27.34% SiO_2 and 8.05% Na_2O) (Kadvani Chemicals, India) were of commercial grade. All the solvents were of analytical quality and were dried by standard methods before use.

^1H and ^{13}C 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 Kα ($\lambda = 1.5405$ Å) radiation with 2θ step size of 0.02° and step time of 5 s of curved Cu Kα 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 °C min^{-1} in flowing N_2.

BET surface area was determined using N_2 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 N_2 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 K_2CO_3 (5.67 g, 41.13 mmol) and methyl iodide (5.83 g, 41.13 mmol) and the mixture was heated at reflux under dry condition for 18 h. After cooling, the volatiles were removed under vacuum and the residual solid was dissolved in CH_2Cl_2 (175 ml) and H_2O (150 ml). The aqueous layer was further extracted with CH_2Cl_2 (3× 60 ml). The combined organic layer was dried over anhydrous Na_2SO_4. 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, $CDCl_3$) δ 3.75 (s, 6H), 6.94 (d, $J = 9.2$ Hz, 1H), 7.11 (d, $J = 9.2$ Hz, 1H), 7.18–7.27 (m, 3H), 7.47 (d, $J = 9$ Hz, 2H), 7.84 (d, $J = 6.6$ Hz, 1H), 7.89 (d, $J = 5.7$ Hz, 1H), 7.95 (d, $J = 10.8$ Hz, 1H), 8.01 (d, $J = 2.8$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 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. $C_{22}H_{17}BrO_2$: 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% SiO_2 and 8.05% Na_2O) was used as a silica source and cetyltrimethylammonium bromide (CTAB) as a template. Precursor gel of composition $1SiO_2$:$0.33Na_2O$:0.5CTAB:$74H_2O$ 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 $CaCl_2$, 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, $CDCl_3$) δ 0.92 (broad t, $J = 7$, 2H), 0.75–0.85