

Research Article

Preparation of Mesoporous SBA-16 Silica-Supported Biscinchona Alkaloid Ligand for the Asymmetric Dihydroxylation of Olefins

Shaheen M. Sarkar,¹ Md. Equb Ali,² Md. Lutfur Rahman,¹ and Mashitah Mohd Yusoff¹

¹ Faculty of Industrial Sciences and Technology, University Malaysia Pahang, 26300 Gambang, Kuantan, Malaysia

² Nanotechnology and Catalysis Research Centre (NanoCat), University of Malaya, Level 3, Block A, IPS Building, 50603 Kuala Lumpur, Malaysia

Correspondence should be addressed to Md. Equb Ali; eaqubali@gmail.com

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Optically active cinchona alkaloid was anchored onto mesoporous SBA-16 silica and the as-prepared complex was used as a heterogeneous chiral ligand of osmium tetroxide for the asymmetric dihydroxylation of olefins. The prepared catalytic system provided 90–93% yield of vicinal diol with 92–99% enantioselectivity. The ordered mesoporous SBA-16 silica was found to be a valuable support for the cinchona alkaloid liganded osmium catalyst system which is frequently used in chemical industries and research laboratories for olefin functionalization.

1. Introduction

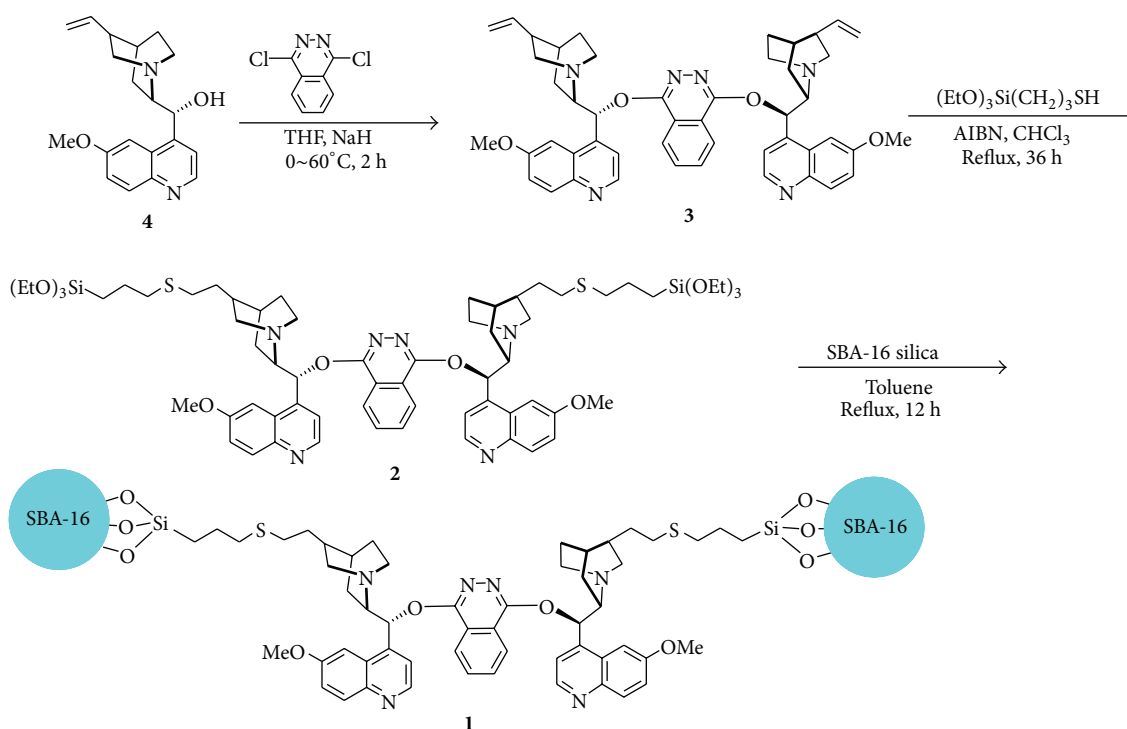
The discovery of highly ordered mesoporous materials has opened up new fields of research in advanced chemistry, modern electronics, and nanotechnology [1–3]. Ordered mesoporous SBA-16 is a nanostructured porous material with a 3D cubic arrangement of mesopores that corresponds to the *Im3m* space group [4–9]. The surface properties of such materials could be significantly modified by adding organic groups and various functionalities onto them [10]. Our interest in the field led us to prepare SBA-16 silica-supported biscinchona alkaloid for osmium-catalyzed asymmetric dihydroxylation (AD) of olefins. Osmium-catalyzed asymmetric dihydroxylation of olefins is an attractive method for the synthesis of optically active diols [11–14]. Cinchona alkaloid-based osmium complexes are harmless and known to be the most effective chiral catalysts for AD reactions in terms of both reactivity and enantioselectivity [15–18].

However, the high cost and toxicity of osmium are a serious concern and many efforts have been devoted to overcome the issue including the development of heterogeneous catalyst ligand to trap the osmium [19, 20]. Immobilization

of homogeneous catalysts onto various supports has emerged as a major route to prepare heterogeneous catalysts [21, 22]. Such a heterogeneous catalyst system offers practical advantages in catalyst separation and potential recycling over its homogeneous counterpart [23, 24]. Silica gel such as mesoporous silica MCM-41 and SBA-15 has been successfully used as inorganic supports for the immobilization of homogeneous catalysts [25–27]. However, despite having highly ordered mesopores, SBA-16 silica has been scarcely explored in this area. Herein, we described the synthesis of SBA-16 supported cinchona alkaloid ligand and tested it for the osmium catalyzed AD reaction of olefins to diols, a key reaction in organic synthesis.

2. Experimental Details

2.1. Preparation of the SBA-16 Silica. SBA-16 silica was synthesized at room temperature under acidic condition using Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, $M_w = 12.6\text{ K}$) as a structure-directing agent (SDA) [28]. The acidic solution was made by adding 1.5 g of deionized (DI) water to 120 g of



SCHEME 1: Preparation of SBA-16-supported biscinchona alkaloid **1**.

2 M HCl solution at room temperature. Subsequently, 8.5 g of tetraethoxysilane (TEOS) was added onto the solution and stirring continued for 20 h. The reaction mixture was kept at 100°C for 48 h. During this time the solid SBA-16 was produced under static conditions in a Teflon-lined vessel. The solid product was recovered and washed with DI water. Calcination was carried out slowly by increasing temperature from room temperature to 500°C in 8 h and heating at 500°C for another 6 h.

2.2. Preparation of the 1,4-Bis(9-O-quininyl)phthalazine 3. NaH (2.24 mmol) at 0°C was slowly added to a stirred solution of 1,4-dichlorophthalazine (0.5 mmol) and quinine **4** (1.15 mmol) in THF (8 mL). The solution was stirred at 60°C for 2 h and then it was quenched at 0°C by careful addition of water. The mixture was extracted in ethyl acetate (EtOAc) and the solvent was removed under reduced pressure. The residue was purified by short column chromatography to separate 1,4-bis(9-O-quininyl)phthalazine **3** and 82% yield was obtained.

2.3. Preparation of the Triethoxysilanized 1,4-Bis(9-O-quininyl)phthalazine 2. 1,4-Bis(9-O-quininyl)phthalazine **3** (0.5 mmol) was added to a solution of (3-mercaptopropyl) triethoxysilane (1.25 mmol) and α,α' -azoisobutyronitrile (AIBN) (0.10 mmol) in degassed chloroform (10 mL) under N₂ atmosphere. The reaction mixture was refluxed for 30 h and concentrated under reduced pressure. The residue was purified by flash short column on silica gel to give compound **2** with 80% yield.

2.4. Immobilization of Biscinchona Alkaloid 2 onto SBA-16 Silica 1. SBA-16 silica (1.0 g) was suspended in toluene and refluxed with compound **2** (145 mg, 0.124 mmol). After 12 h, the powder was collected by filtration and washed with methanol and methylene chloride. After drying under vacuum at 70°C, SBA-16-supported alkaloid **1** (1.077 g) was obtained. Elemental analysis and weight gain showed that 0.073 mmol of 1,4-bis(9-O-quininyl)phthalazine was anchored on 1.0 g of SBA-16-supported chiral Ligand **1**.

2.5. Characterization of SBA-16-Supported Chiral Ligand 1. Powder X-ray diffractometry (Philips PW 1729) was used for the determination of crystalline structure using Cu K_α radiation over $0.5^\circ \leq 2\theta \leq 3^\circ$. The XRD sample of SBA-16 was analyzed at 30°C. The diffractograms showed 3 peaks at $2\theta \approx 0.74^\circ, 1.1^\circ, \text{ and } 1.4^\circ$ that corresponded to (110), (200), and (211) planes, respectively, in the cubic *Im3m* structure. The transmission electron microscopy (TEM) was performed with a FEI Tecnai G² microscope operated at 200 kV. The TEM sample was prepared by placing a few drops of SBA-16 powder dispersed in acetone on a carbon grid and allowing it to dry for 5 min before TEM analysis. Large particles were crushed by submerging them in liquid nitrogen followed by mechanical grinding in a mortar prior to acetone dispersion. The nitrogen adsorption-desorption measurements were performed at -196°C on a Micromeritics ASAP 2020 surface area and porosity analyzer. Approximately 0.5 g of SBA-16 was degassed at 300°C for 9 h before taking the measurement. The surface area determination was performed by the Brunauer-Emmett-Teller (BET) method [29] over the relative pressure

(P/P_0) range of 0.05–0.2. The pore-size distribution was determined using the Broekhoff-de Boer (BdB) method [30] applied to the adsorption branch. Finally, the total pore volume was calculated from the amount of adsorbed N_2 at $P/P_0 = 0.99$, and the microporous volume was determined using the t -plot method.

2.6. Asymmetric Dihydroxylation of Olefin Using SBA-16-Supported Chiral Ligand 1. A mixture of SBA-16-supported biscinchona alkaloid **1** (1 mol%), potassium ferricyanide (1.5 mmol), potassium carbonate (1.5 mmol), and OsO_4 (1 mol%, 0.5 M in water) in *tert*-butyl alcohol-water (6 mL, 1:1, v/v) was stirred at room temperature for 30 min. Olefin (0.5 mmol) was added at once and stirred for 7–15 h. The reaction mixture was diluted with water and CH_2Cl_2 and the immobilized Ligand **1** was separated by filtration. The crude product was purified by flash column chromatography, and the enantiomeric excess of the diol was determined by chiral gas chromatography (GC) analysis (Agilent HP Chiral-20B 30MX0.25MMX0.25UM GC Column).

3. Results and Discussion

To synthesize a SBA-16-supported biscinchona alkaloid **1**, we started with quinine and 1,4-dichlorophthalazine following a route shown in Scheme 1.

Treatment of optically active quinine **4** with 1,4-dichlorophthalazine in the presence of excess NaH synthesized 4-bis(9-*O*-quininyl)phthalazine **3** with high yield (82%). Radical reaction of dimeric quinine **3** with (3-mercaptopropyl)triethoxysilane in the presence of AIBN radical initiator provided compound **2** having a pendant triethoxysilane functional group. The desired immobilized biscinchona alkaloid SBA-16 **1** (loading ratio: 0.073 mmol/g) was readily obtained by condensation of **2** with surface silanols of SBA-16 support in refluxing toluene. The degree of functionalization was determined by elemental analysis and weight gain. As shown in Table 1, the surface area and pore diameter were decreased following the modification. The high resolution transmission electron microscopy (HRTEM) image of SBA-16-supported Ligand **1** is shown in Figure 1. The 3D cubic structure and the pore arrays were conserved after the immobilization of 1,4-bis(9-*O*-quininyl)phthalazine onto SBA-16 silica and it was also confirmed by XRD (Figure 2).

The AD reaction of stilbene was performed in the presence of immobilized cinchona alkaloid **1** (1 mol%) and OsO_4 (1 mol%) at room temperature. Potassium carbonate and potassium ferricyanide were used as a secondary oxidant in *tert*-butyl alcohol-water mixture (1:1). The results are summarized in Table 2. Surprisingly, catalytic AD reactions of stilbene provided excellent enantioselectivities and high yields (entries 1 and 2). Osmium catalyst loading of 0.5 mol% was sufficient to obtain outstanding enantioselectivity as well as high reactivity. Moreover, the SBA-16-supported alkaloid- OsO_4 complex could be reused for the AD reaction of stilbene without a significant loss of reactivity and enantioselectivity (entry 3). The catalyst was also highly effective to

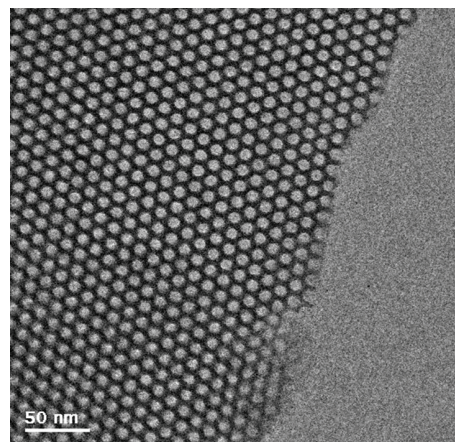


FIGURE 1: HRTEM image of SBA-16-supported Ligand **1**.

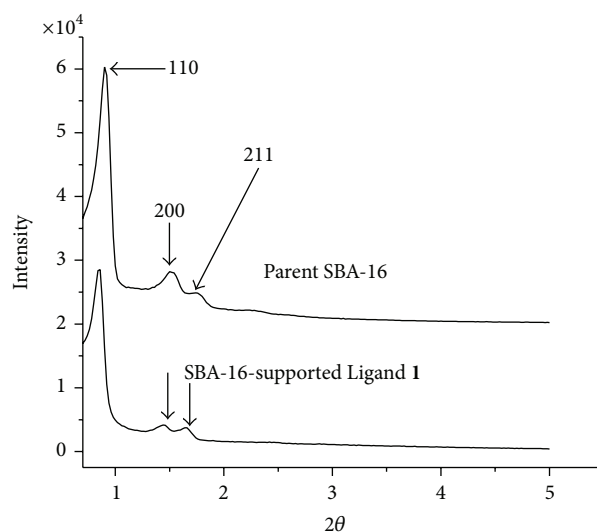


FIGURE 2: XRD pattern of SBA-16-supported Ligand **1**.

AD of methylcinnamate, 1-phenyl-1-cyclohexene, and styrene (entries 4–6).

The SBA-16-supported Ligand **1** reported here showed somewhat higher reactivity and better asymmetric induction over amorphous silica-supported biscinchona alkaloid [25]. The improved outcome of the reaction seems to be attributed to the ordered array of chiral catalytic site on the nanopore surface of SBA-16 support. The ordered array leads to elegant site isolation which may result in enhanced enantioselectivity.

Romero et al. [31] reported the asymmetric dihydroxylation reaction of olefin using ionic liquid, which involves high cost and toxicity. The yield and enantioselectivity of the styrene were also very poor (87% yield, 62% ee) [32]. On the other hand, Junttila and Hormi [33] used methanesulfonamide as an accelerator of the asymmetric dihydroxylation reaction using potassium osmate (vi) and obtained 97% ee with low yield (70%) of the diol product. It is noteworthy here that the alkaloid ligand complexes synthesized in this report produced excellent results in terms of both yield (93%) and enantioselectivity (92–99%).

TABLE 1: Structural characteristics of SBA-16-supported Ligand 1.

Sample	Surface area	Pore diameter	Pore volume	Functional group
SBA-16	820 m ² /g	5.13 nm	0.73 cm ³ /g	—
1	490 m ² /g	3.68 nm	0.45 cm ³ /g	0.073 mmol/g

TABLE 2: Heterogeneous AD of olefins using SBA-16-supported Ligand 1^a.

Entry	Olefin	Time (h)	Yield (%)	(%) Ee ^b	Config. ^b
1		7	93	>99	S, S
2 ^c		7	91	98	S, S
3 ^d		8	90	97	S, S
4		9	91	96	2R, 3S
5		10	92	94	2S, 3S
6		15	92	92	S

^aThe reactions were carried out at RT; molar ratio of olefin/OsO₄/supported ligand = 1/0.01/0.01. ^bEe and absolute configuration were determined by chiral GC analysis. ^cMolar ratio of olefin/OsO₄/supported ligand = 1/0.005/0.005. ^dReaction was carried out with regenerated 1 without further addition of OsO₄.

4. Conclusion

We successfully synthesized air and moisture stable SBA-16-supported bisquinchona alkaloid chiral ligand. Osmium tetroxide readily formed a chiral complex with the SBA-16-supported bisquinchona alkaloid at room temperature. The synthesized SBA-16 supported Os-complex efficiently promoted the asymmetric dihydroxylation of olefin to corresponding diols with 92–99% enantioselectivity and 93% yield, demonstrating SBA-16 silica as an excellent support material for the heterogeneous chiral ligand.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

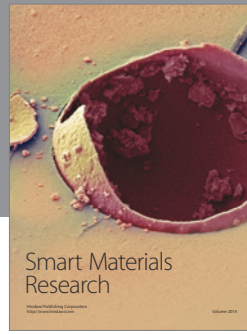
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