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Siliceous mesocellular foam-supported chiral bisoxazoline: Application to asymmetric cyclopropanation

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Abstract

Chiral bisoxazolines were covalently immobilized onto siliceous mesocellular foams (MCF) by a simple method. The heterogenized bisoxazoline-copper catalysts showed high enantioselectivity (up to 85% enantiomeric excess (ee)) and excellent recyclability in asymmetric cyclopropanation reactions.

Keywords: Bisoxazoline; Mesoporous; Cyclopropanation; Immobilization

1. Introduction

Chiral bisoxazolines have been used in various asymmetric catalytic reactions [1]. They can be synthesized easily from chiral aminoalcohols, which are derived from amino acids. Recently, several new asymmetric reactions by chiral bisoxazolines have been reported [2], showing that these catalysts are very useful. However, these ligands are expensive, and high catalyst-to-substrate ratios are required to achieve good enantioselectivities and reactivities.

Several research groups have reported on heterogenizing chiral bisoxazolines [3]. Most heterogenized bisoxazolines are polymer-supported [4,5], although a few silica-supported bisoxazolines [6–8] have been reported. Silica-supported catalysts are more easily recycled, and have better stability than polymer-supported catalysts. However, silica has a high density of surface silanol groups, which can adversely impact the catalytic reactions [7,8], and silica is a more difficult support for the covalent immobilization of ligands.

Nitrogen-containing chiral ligands, such as chiral bisoxazolines, have a low Rf value on TLC plate. This indicates a strong interaction between the ligands and silica surface. After ligand immobilization, the strong interaction between ligand and silica surface may impact the formation of metal complexes, leading to low enantioselectivity. Some previous studies showed that capping of free silanol groups after immobilization of chiral ligands improved the enantioselectivity and regioselectivity by preventing strong interaction between the ligands and silanol groups [7,8].

Herein, we report the immobilization of chiral bisoxazolines onto MCF, which is a stable mesoporous silica with interconnected pores [9]. The effect of capping the free silanol groups on the MCF support, and the role of linker group in immobilizing the bisoxazoline ligand onto MCF were investigated.

2. Experimental

2.1. General

MCF, MCM-48, and SBA-15 were synthesized according to the literature procedures [9,10]. A commercial silica (60 Å pores, BET surface area ~500 m^2/g, pore volume = 0.75 cm^3/g) was purchased from Aldrich. Other chemicals were purchased from commercial suppliers, and were used without further purification. *Tert*-butyl-bisoxazolines (tBBOX) (**1**), anhydrous tetrahydrofuran (THF), anhydrous toluene, anhydrous CH_2Cl_2, styrene, phenylhydrazine and ethyldiazoacetate (EDA) were purchased from Aldrich. 3-Iodopropyltrimethoxysilane and [(chloromethyl)phenylethyl]trimethoxysilane were purchased

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from Gelest Inc. Photoacoustic Fourier-transform infrared (PA-FTIR) spectra were obtained with a MTEC Model 200 photoacoustic cell on a Bio-Rad FTS-60A spectrometer.

2.2. Preparation of MCF-supported bisoxazoline

2.2.1. Preparation of **2**

n-Butyllithium (*n*-BuLi) (1.6 M in hexane, 980 μL, 1.57 mmol) was added to a solution of tBBOX (**1**) (209 mg, 0.78 mmol), diisopropylamine (*i*-Pr_2NH) (110 μL, 0.78 mmol, 1 equiv.) and tetramethylethylenediamine (TMEDA) (237 μL, 1.57 mmol, 2 equiv.) in THF (15 mL) at −78 °C [11]. The reaction mixture was warmed to −20 °C and stirred for 1 h. The solution was cooled down to −78 °C, and 3-iodopropyltrimethoxysilane (309 μL, 1.57 mmol, 2 equiv.) was added dropwise. The mixture was warmed to room temperature and stirred for 3 days, after which the solvent was evaporated under vacuum. Toluene was added, and the soluble portion was collected by centrifuge and washed with toluene. The solution was added to MCF (1.5 g), which had been dried under vacuum at 180 °C for 1 day. The suspension was stirred at 80 °C for 3 days, filtered through a filter funnel, and washed with toluene (3 × 20 mL), acetone (3 × 20 mL), water (10 × 20 mL), methanol (3 × 20 mL) and CH_2Cl_2 (3 × 20 mL). After drying in vacuum, the desired product (**2**) was obtained.

- PA-FTIR (cm^{-1}): 3427, 2958, 1659, 1085, 809, 459.
- Elemental analysis: C: 11.07%; H: 1.42%; N: 1.21%.
- Loading of tBBOX: 0.432 mmol/g.

2.2.2. Preparation of **3**

Methyllithium (MeLi) (1.4 M in ether, 2.27 mL, 3.18 mmol, 2.1 equiv.) was added to a solution of tBBOX (403 mg, 1.51 mmol) in THF (20 mL) at −50 °C. After stirring the mixture at −50 °C for 1 h, [(chloromethyl)phenylethyl]trimethoxysilane (743 μL, 3.02 mmol, 2 equiv.) was added dropwise. The mixture was stirred at room temperature for 2 h, and then heated to 50 °C. It was stirred at 50 °C for 3 days, and the solvent was evaporated under vacuum. Toluene was added, and the toluene phase was collected by centrifugation and washing. The resulting solution was added to MCF (3.0 g), which had been dried under vacuum at 180 °C for 1 day. The suspension was stirred at 80 °C for 3 days, filtered through a filter funnel, and washed with toluene (3 × 20 mL), acetone (3 × 20 mL), water (10 × 20 mL), methanol (3 × 20 mL) and CH_2Cl_2 (3 × 20 mL). After drying in vacuum, the desired product (**3**) was obtained.

- PA-FTIR (cm^{-1}): 3381, 2958, 1656, 1608, 1085, 807, 459.
- Elemental analysis: C: 12.54%; H: 1.28%; N: 0.91%.
- Loading of tBBOX: 0.325 mmol/g.

2.2.3. Capping of free silanol groups with hexamethyldisilazane (HMDS) (**4** and **5**)

Catalyst **2** or **3** (700 mg) was dried at 80 °C for 2 days. Excess HMDS (700 μL) was added to the dried catalyst in hexane (10 mL). The suspension was stirred at room temperature for 2 days, filtered through a filter funnel, and washed with hexane (3 × 10 mL), acetone (3 × 10 mL), methanol (3 × 10 mL) and CH_2Cl_2 (3 × 10 mL). After drying in vacuum, the desired product (**4** or **5**) was obtained.

Catalyst **4**: PA-FTIR (cm^{-1}): 3449, 2957, 1663, 1089, 842, 811, 460; elemental analysis: C: 13.25%; H: 1.98%; N: 1.09%; loading of tBBOX: 0.389 mmol/g.

Catalyst **5**: PA-FTIR (cm^{-1}): 3443, 2958, 1663, 1608, 1089, 844, 809, 459; elemental analysis: C: 14.92%; H: 1.88%; N: 0.84%; loading of tBBOX: 0.300 mmol/g.

2.3. Preparation of bisoxazoline supported on other silica supports

2.3.1. Immobilization of the chiral bisoxazoline

The same procedure described for **2** was followed, except that the conventional silica supports were activated by refluxing them in 1.0 M aq. HCl solution for 6 h. PA-FTIR spectra of these silica-supported catalysts were similar to that of the MCF-supported catalyst.

Elemental analysis:

- MCM-48-supported bisoxazoline: C: 3.32%; H: 0.42%; N: 0.34%.
- SBA-15-supported bisoxazoline: C: 9.01%; H: 1.17%; N: 0.98%.
- Commercial silica-supported bisoxazoline: C: 6.97%; H: 0.96%; N: 0.76%.

Loading of tBBOX:

- MCM-48-supported bisoxazoline: 0.12 mmol/g.
- SBA-15-supported bisoxazoline: 0.35 mmol/g.
- Commercial silica-supported bisoxazoline: 0.27 mmol/g.

2.3.2. Capping of free silanol groups with HMDS

The same procedure described for **4** was followed for the silica-supported bisoxazoline catalysts. The PA-FTIR spectra of the post-capped catalysts were similar to that of **4**.

Elemental analysis:

- MCM-48-supported bisoxazoline: C: 7.28%; H: 1.03%; N: 0.31%.
- SBA-15-supported bisoxazoline: C: 12.54%; H: 1.62%; N: 0.87%.
- Commercial silica-supported bisoxazoline: C: 10.72%; H: 1.53%; N: 0.71%.

Loading of tBBOX:

- MCM-48-supported bisoxazoline: 0.11 mmol/g.
- SBA-15-supported bisoxazoline: 0.31 mmol/g.
- Commercial silica-supported bisoxazoline: 0.25 mmol/g.

2.4. Cyclopropanation

$(CuOTf)_2$·toluene (0.011 mmol) or $Cu(OTf)_2$ (0.022 mmol) was added to the immobilized bisoxazolines (0.022 mmol) in

CH_2Cl_2 (4 mL). The mixture was stirred at room temperature for 5 days. In the case of $Cu(OTf)_2$, phenylhydrazine (50 μL of a 5% solution) was added. After addition of styrene (153 μL, 1.32 mmol), a solution of EDA (1.1 mmol, diluted with 2 mL of CH_2Cl_2) was added over 5 h using a syringe pump. The mixture was stirred for 2 h and then centrifuged. The solution portion was collected, and the *trans*/*cis* ratio and yield were determined by gas chromatography (GC). The ee value was determined by GC using a Cyclodex-B column. The precipitate was washed with CH_2Cl_2 (10 mL), and then centrifuged three times. The recovered catalyst was reused directly for the next run.

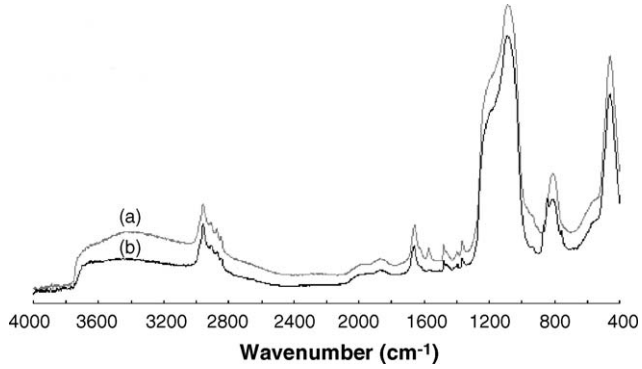


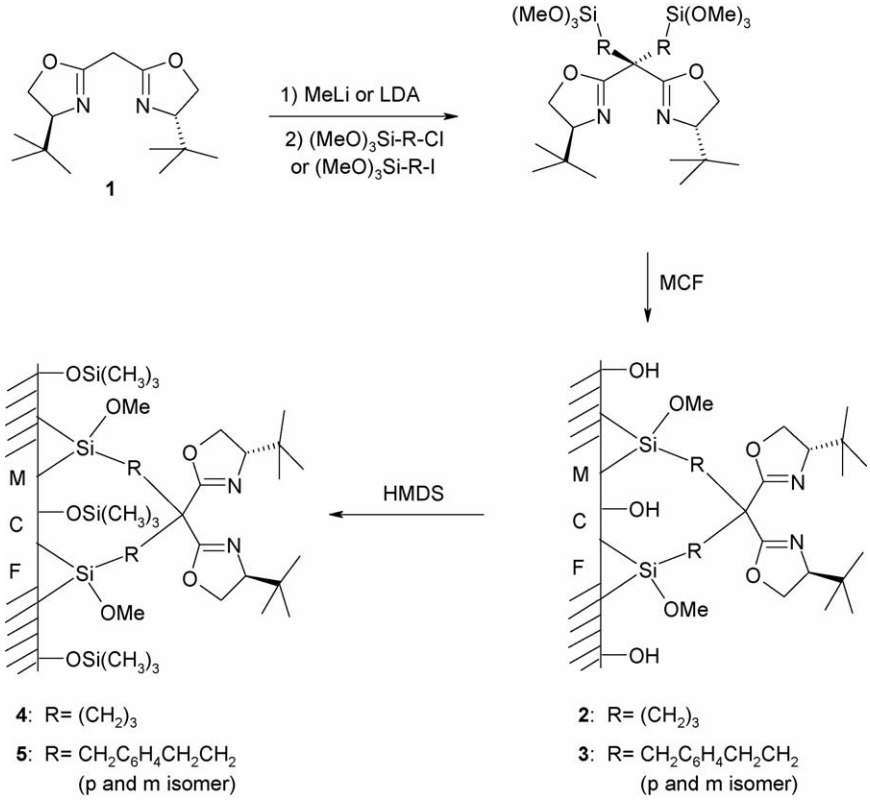
Fig. 1. PA-FTIR spectra of (a) **2** and (b) **4**.

3. Results and discussion

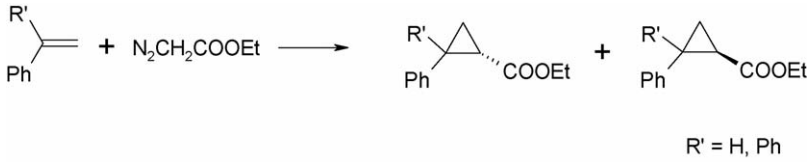
MCF was templated by triblock copolymers, and its pore size can be easily controlled by the amounts of mesitylene (TMB) and fluoride (e.g. ammonium fluoride). It has a high surface area (∼800 m^2/g), and open pores of ∼25 nm that were interconnected by windows of ∼11 nm [9]. MCF's ultralarge pore size and 3D pore structure were well suited for fixating bulky complexes, and for catalyzing reactions involving large substrates [12].

The two protons on the methylene bridge of commercial *tert*-butyl-bisoxazolines (tBBOX **1**, Aldrich) were deprotonated by MeLi or lithium diisopropylamide (LDA) [5,6,11]. The deprotonated bisoxazolines were reacted with electrophilic silane agents, such as 3-iodopropyltrimethoxysilane [6] and [(chloromethyl)phenylethyl]trimethoxysilane to give T-silyl-functionalized bisoxazolines (where T referred to the T-type silicon atom with three oxygen neighbors) (Scheme 1). These modified bisoxazolines were easily immobilized onto MCF by heating in toluene, and high loadings (0.3–0.4 mmol/g) of the modified ligands were achieved. Reactive silanol groups were capped with trimethylsilyl (TMS) groups by reacting with HMDS. The capping of free silanols with TMS groups after immobilization of bisoxazolines resulted in a decreased Si-*OH* stretching at ∼3400 cm^{-1} on the PA-FTIR spectrum (Fig. 1).

Copper complexes of the heterogenized bisoxazolines were formed by reacting with $(CuOTf)_2$·toluene or $Cu(OTf)_2$ in CH_2Cl_2 for 3 days. The resulting catalysts were used for



Scheme 1. Immobilization of chiral bisoxazolines onto MCF.



Scheme 2. Cyclopropanation of styrene or diphenylethylene with EDA.

asymmetric cyclopropanation reactions. This immobilization method provided several advantages over the previously reported method [6] in terms of silanol protection, removal of impurities (such as lithium and iodine) by a washing process after immobilization, and coordination of various metals to the immobilized bisoxazoline ligands.

First, the influence of silanol groups on the catalyst's enantioselectivity and reactivity in cyclopropanation (Scheme 2) was tested by physically mixing homogeneous **1**:CuOTf catalyst (0.022 mmol) with calcined MCF (150 mg, "MCF") and TMS-capped MCF (150 mg, "TMS–MCF"). The mixture of **1**:CuOTf and MCF gave 9% lower ee for the *trans*-isomer and a lower *trans*/*cis* selectivity (64/36) than the mixture of **1**:CuOTf and TMS-MCF, which showed the same % ee for the *trans*-isomer (90%) and *trans*/*cis* selectivity (73/27) as the homogeneous **1**:CuOTf catalyst (see Table 1). The recovered MCF was subjected to thorough washing with dichloromethane before the second run, which gave a moderate yield (66%) and ee for the *trans*-isomer (60%). After the second run, 0.083 mmol Cu/g was found by elemental analysis to have remained on the surface of MCF. The free silanol groups on MCF might have acted as sites for anchoring the homogeneous catalysts in a similar manner as in clays; such interaction with MCF might have caused the catalyst's enantioselectivity and regioselectivity to be reduced [6]. In the case of TMS–MCF, a very small amount of **1** (0.017 mmol Cu/g) remained on the support surface after the second run. Most of the homogeneous catalysts was left in the reaction medium in the first run, only a small amount of **1**:CuOTf was adsorbed on the recovered TMS–MCF, resulting in a low yield (49%) and a poor enantioselectivity (28% ee *trans*) (see Table 1). This study indicated that capping of reactive silanol groups would be important towards minimizing interaction between the catalyst and the siliceous support.

Next, MCF was used to immobilize bisoxazoline-Cu(I) catalysts. The MCF-supported catalyst (**2**:CuOTf) gave a lower ee for the *trans*-isomer (76%) than the catalyst supported on TMS-capped MCF (**4**:CuOTf) (84%) (see Table 2). The large amount of free silanol groups in the uncapped MCF negatively impacted the catalyst's enantioselectivity in **2**:CuOTf.

To covalently immobilize bisoxazolines, two types of linker groups were used, a propyl group and a methylphenylethyl group. Two Cu sources, CuOTf and $Cu(OTf)_2$, were employed in the ligand–copper complexes. The ligand–$Cu(OTf)_2$ complexes

Table 1
Cyclopropanation of styrene with EDA catalyzed by homogeneous catalysts (**1**:CuOTf and **1**:$CuOTf_2$), and a mixture of a homogeneous catalyst and MCF or TMS–MCF[a]

Catalyst	Run #	% Yield[b]	*Trans*/*cis*[c]	% ee *trans*[d]	% ee *cis*[d]
1:CuOTf	1	88	73/27	90	82
1:$Cu(OTf)_2$[e]	1	83	72/28	85	80
1:CuOTf + MCF	1	71	64/36	81	70
	2	66	59/41	60	55
1:$Cu(OTf)_2$[e] + MCF	1	85	65/37	74	62
1:CuOTf + TMS–MCF	1	87	73/27	90	82
	2	49	63/37	28	27
1:$Cu(OTf)_2$[e] + TMS–MCF	1	81	71/29	85	75

[a] Styrene/EDA ratio = 1.2 and 2 mol% Cu at room temperature for 7 h (dropwise addition of EDA for 5 h and stirring for an additional 2 h).
[b] Calculated from GC calibration curve between *n*-decane and product.
[c] Determined by GC.
[d] Determined by GC with a Cyclodex-B column.
[e] Reduced by phenylhydrazine before use.

Table 2
Cyclopropanation of styrene with EDA catalyzed by the heterogenized catalysts[a]

Catalyst	Run #	Styrene/EDA	% Yield[b]	*Trans*/*cis*[c]	% ee *trans*[d]	% ee *cis*[d]
2:CuOTf	1	1.2	83	57/43	76	69
	2	1.2	80	56/44	76	71
	3	1.2	75	55/45	77	72
	4	1.2	88	54/46	78	72
4:CuOTf	1	1.2	85	60/40	84	79
	2	1.2	82	58/42	85	80
	3	1.2	79	58/42	84	80
	4	1.2	81	57/43	83	79
4:CuOTf	1	3.0	85	60/40	85	80
	2	3.0	93	59/41	83	79
	3	3.0	90	58/42	83	79
	4	3.0	86	57/43	84	80
4:$Cu(OTf)_2$[e]	1	1.2	78	60/40	81	78
	2	1.2	86	59/41	82	79
	3	1.2	81	58/42	84	79
	4	1.2	74	57/43	85	80
5:CuOTf	1	1.2	80	49/51	73	69
	2	1.2	78	50/50	74	68
	3	1.2	77	51/49	73	68
	4	1.2	76	51/49	72	67
5:$Cu(OTf)_2$[e]	1	1.2	78	49/51	70	67
	2	1.2	84	50/50	71	67
	3	1.2	84	50/50	71	65
	4	1.2	86	50/50	71	66

[a] 2 mol% Cu at room temperature for 7 h (dropwise addition of EDA for 5 h and stirring for an additional 2 h).
[b] Calculated from GC calibration curve between *n*-decane and product.
[c] Determined by GC.
[d] Determined by GC with a Cyclodex-B column.
[e] Reduced by phenylhydrazine before use.

were reduced by phenylhydrazine before the catalytic testing. The propyl-linked catalyst (**4**) gave better enantioselectivities and higher *trans*/*cis* ratio than the bulkier methylphenylethyl-linked catalyst (**5**) (see Table 2).

The same bisoxazoline (tBBOX) ligand was immobilized on silica support by reacting with mercaptopropyltrialkoxysilane under a radical reaction condition [5]. The silica-immobilized tBBOX with a sulfide linkage gave poor enantioselectivities in asymmetric cyclopropanation. MCF-supported tBBOX prepared with the sulfide linkage also showed a very poor enantioselectivity (<15% ee for the *trans*-isomer). These findings indicated that the linker group played an important role in achieving high enantioselectivity in heterogenized bisoxazoline catalysts.

4:CuOTf gave similar ee values for the *trans*-isomer (83–85%) over four runs (see Table 2). High styrene/EDA ratio (3) was found to lead to a higher yield for **4**:CuOTf after the initial run. **4**:Cu(OTf)$_2$ gave a slightly lower ee for the *trans*-isomer (81%) in the initial run, but this ee value improved with recycling to 85% in run #4. Homogeneous catalyst **1**:Cu(OTf)$_2$ also gave a lower ee for the *trans*-isomer (85%) than **1**:CuOTf (90%) (Table 1).

Recycling of CuOTf complexed with **4** and **5** showed insignificant variations in enantioselectivities and *trans*/*cis* ratios (Table 2). After four runs, **4**:CuOTf showed a slight loss in Cu (<7%) and a 4% increase in carbon. The latter might be due to excess reactants or side-products coordinated to the copper catalyst or adsorbed onto the MCF surface. **4**:CuOTf was also examined for the cyclopropanation of diphenylethylene with EDA (Table 3). It demonstrated a consistently high ee value of 82% and 83% in runs #1 and #2.

2:CuOTf showed a slight increase in ee values with recycling (Table 2). The side-products might have capped the silanol groups in this case. These results were contrary to those reported previously [6], which gave a slight decrease in ee values with recycling.

Cyclopropanation catalyzed by bisoxazoline–Cu(II) complexes was reported to require long reaction times and sometimes high temperatures for initiation, and gave low yields [4,13]. However, cyclopropanation over the heterogenized **4**:Cu(OTf)$_2$ catalyst without the addition of phenylhydrazine still provided 82% ee for the *trans*-isomer, and a high yield (80%) under the same reaction time as bisoxazoline–Cu(I) at room temperature (see Fig. 2). Good enantioselectivities and high yields were successfully retained over eight runs for this system.

For comparison, the modified bisoxazoline was also immobilized on other silica supports, which were subsequently capped

Table 3
Cyclopropanation of diphenylethylene with EDA catalyzed by **4**:CuOTf[a]

Run #	Diphenylethylene/EDA	% Yield[b]	% ee[c]
1	2.0	82	82
2	2.0	80	83

[a] 2 mol% Cu at room temperature for 7 h (dropwise addition of EDA for 5 h and stirring for an additional 2 h).
[b] Isolated yield.
[c] Determined by HPLC with a chiral OD-H column, hexane/isopropanol = 99.4:0.6.

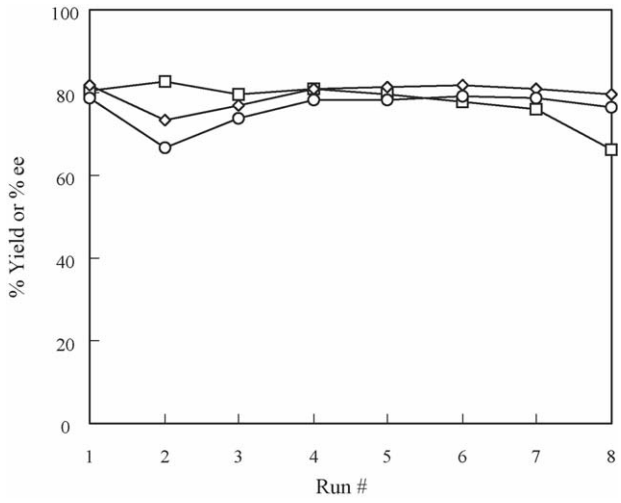


Fig. 2. (□) Yield, and ee for (◊) *trans*- and (○) *cis*-isomers for the cyclopropanation of styrene with EDA over **4**:Cu(OTf)$_2$ without phenylhydrazine.

with HMDS. Compared to **4**:CuOTf, which has a tBBOX loading of 0.389 mmol/g, the tBBOX loadings on MCM-48 (0.11 mmol/g), SBA-15 (0.31 mmol/g), and commercial silica (0.25 mmol/g) were lower. These could be attributed to the smaller pore sizes of the other silica supports, especially that of MCM-48 (~3.2 nm).

Asymmetric cyclopropanation of styrene was conducted over the silica-supported catalysts under the same conditions as **4**:CuOTf in Table 2 (styrene/EDA = 1.2). Similar ee values for *trans*-isomer were attained with the bisoxazoline catalysts supported on MCM-48 (81%), SBA-15 (83%), and commercial silica (82%), compared to **4**:CuOTf (84%). This illustrated that the immobilization scheme and the capping of silanol groups presented in this work were applied effectively towards achieving high enantioselectivities for chiral bisoxazoline catalysts immobilized on different types of porous silica supports.

Much lower yields were attained by bisoxazoline supported on MCM-48 (62%), SBA-15 (80%), and commercial silica (72%), compared to **4**:CuOTf (85%). In all cases, 100% conversion was achieved, but greater chemoselectivity for the desired reaction between styrene and EDA (versus the undesired reaction between two EDA molecules) was attained by the MCF-supported catalyst likely due to the facilitated diffusion of the relatively bulky styrene made possible by the ultralarge, open, interconnected pores of MCF. While SBA-15 and commercial silica have similar pore sizes (~6.5 nm versus 6.0 nm), the former has uniform, cylindrical pores, while the latter has a relatively broad pore size distribution. The finer pores in commercial silica could have led to diffusion limitations, giving rise to the lower yield in the commercial silica-supported catalyst compared to that of SBA-15-supported catalyst.

4. Conclusions

In conclusion, the two-step T-silyl functionalization of bisoxazolines by lithiation at the methylene bridge, followed by reaction with electrophilic silanes represented a simple and effective method for immobilizing bisoxazoline ligands onto the surface

of siliceous MCF and other silica supports. The resulting heterogenized Cu-bisoxazoline catalysts demonstrated high enantioselectivities, excellent yield, and good recyclability for asymmetric cyclopropanation reactions. The capping of free silanol groups on the silica surface was found to be important towards achieving high enantioselectivities. The linker group used in the covalent immobilization of bisoxazolines onto the siliceous support was also important towards optimizing the enantioselectivity and yield of the heterogenized catalysts.

Acknowledgments

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