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Research Article

Preparation of Mesoporous Silica-Supported Chiral Amino Alcohols for the Enantioselective Addition of Diethylzinc to Aldehyde and Asymmetric Transfer Hydrogenation to Ketones

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Optically active (−)-ephedrine, (−)-norephedrine, and (−)-prolinol were immobilized onto cubic mesoporous MCM-48 silica. The immobilized amino alcohols served as a heterogeneous chiral catalyst for the asymmetric addition of diethylzinc to aldehydes and transfer hydrogenation to ketones. The developed catalytic process yielded optically enriches secondary aromatic alcohols with 92–99% conversion and 70–82% enantioselectivity.

1. Introduction

Synthesis of optically active secondary alcohols through the asymmetric addition of organozinc reagent to aldehydes and transfer hydrogenation of ketones is an important chemical process in industry and drugs' synthesis research [1–10]. Reduction of carbonyl group into alcohols involves a number of reducing reagents including addition of alkyl group, molecular hydrogen, metal hydrides, and dissolving metals [11]. The use of the hydrogen donor has some advantages over the use of molecular hydrogen since it avoids risks and constraint associated with hydrogen gas as well as the necessity of pressure controlling vessels and other equipment [12]. In the recent years, covalent immobilization of chiral catalysts onto insoluble supports has attracted much interest [13–17] since it provides an easy separation of products from the catalysts without tedious experimental workup, enabling an efficient recovery of the spent catalyst. It prevents the intermolecular aggregations of the active species because of their rigid structures, which do not swell or dissolve in organic solvents and often exhibit superior thermal and mechanical stability under the catalytic conditions. However, the examples of immobilized catalysts for the asymmetric transfer hydrogenation of ketones have been rare [18, 19]. Further, the immobilization of catalysts onto inorganic supports has been poorly reported [20–22].

The successful development of homogeneous catalysts has sometimes been followed by attempts to attach the catalysts on an insoluble inorganic support [23]. The discovery of ordered mesoporous materials opened a new field for catalyst synthesis. Ordered mesoporous material is one of the attractive inorganic supports in preparing immobilized catalysts. The use of well-defined nanostructured mesoporous materials [24–26], magnetic materials [27], zeolites [28], organic polymers [29], or high surface area carbon [30] for catalytic transformations of organic substrates is an exciting and rapidly growing area. Recently, mesoporous MCM materials with uniform nanosized pore diameters and high specific surface areas have got intense interest as inorganic supports [31–33]. Such immobilization offers practical advantages such as ease of separation and reuse of the catalysts and catalysis within the microenvironment of nanopores. MCM-41 silica has recently been used as a mesoporous support for the immobilization of Au, Pt, Pd, Ni, Co, and Cu catalysts [34, 35]. On the other hand, cubic-structured mesoporous MCM-48 silica has received

less attention due to difficulties in synthesis [36–39]. Owing to its unique three-dimensional pore structure, MCM-48 may be more advantageous than MCM-41. MCM-48 with three-dimensional nanosized pore networks and high specific surface areas would be of high interest in this area. Moreover, organic groups can be robustly anchored to the surface. Attachment of optically active ligands onto the pores of MCM-48 silica can create heterogeneous chiral ligands [40]. Our interest in the field led to prepare MCM-48-supported chiral ligands for asymmetric addition of diethylzinc to aldehydes and asymmetric transfer hydrogenation of ketones. Herein, we describe our results for the asymmetric addition of diethylzinc reagent to aldehydes and transfer hydrogenation to the ketones catalyzed by MCM-48-supported chiral amino alcohol Ru-complex.

2. Experimental

2.1. Preparation of the MCM-48 Silica. MCM-48 silica was prepared according to the procedure described in bibliography [39]. The resultant silicate mixture was stirred for 1 h at room temperature and the samples were then collected by filtration and transferred to a Teflon lined steel vessel. The sample was then heated at 100°C for 4 days. After the mixture was cooled, the precipitated product was washed with DI water and calcinated at 500°C for 8 h. The MCM-48 was characterized by XRD and TEM analyses.

2.2. Preparation of the Chloropropylated MCM-48 Silica **1**. To a stirred solution of (3-chloropropyl)triethoxysilane (1.2 g, 4.98 mmol) in toluene (25 mL) was added fresh calcinated MCM-48 silica (2.4 g) and the mixture was stirred at 105°C for 12 h. The reaction was cooled at room temperature and filtrated. The powder was washed several times with methylene chloride and dried under vacuum at 70°C to give 3-chloropropylated MCM-48 silica **1**. Weight gain showed that 1.1 mmol of (3-chloropropyl)triethoxysilane was immobilized onto 1.0 g of mesoporous MCM-48 silica.

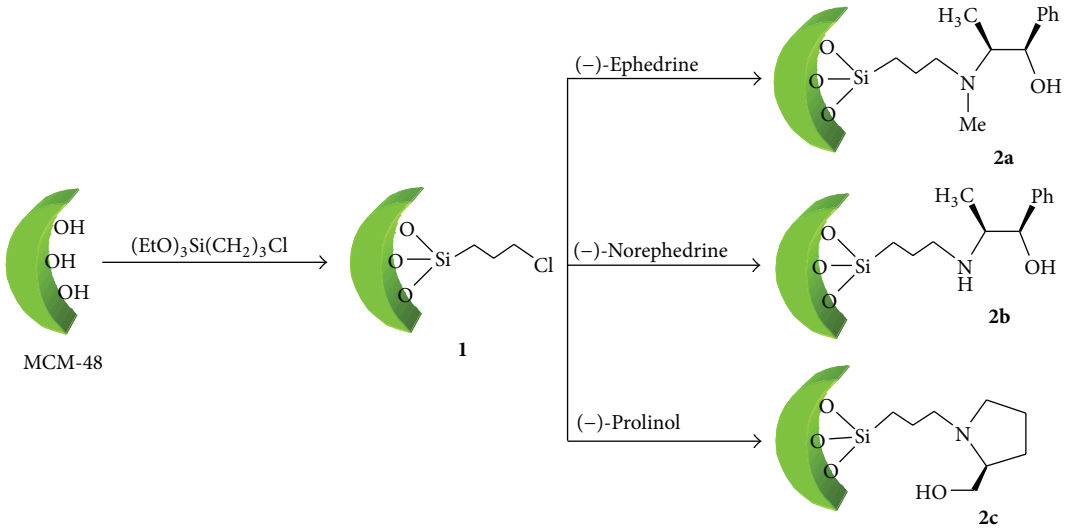
2.3. Preparation of the MCM-48-Supported Chiral Amino Alcohols **2**. To a stirred solution of (−)-ephedrine (0.23 g, 1.38 mmol) and diisopropylethylamine (0.12 g, 0.92 mmol) in toluene (10 mL) was added 3-chloropropylated MCM-48 silica **1** (0.7 g, 0.77 mmol). The mixture was gradually heated at 105°C and allowed to react for 36 h. The powder was collected by filtration and successively washed with H_2O, methanol, and CH_2Cl_2. The MCM-48-supported ephedrine **2a** was obtained after drying in vacuo at 70°C. Elemental analysis and weight gain showed that 0.47 mmol of ephedrine was anchored onto 1.0 g of 3-chloropropyl MCM-48 silica **2a**. Mesoporous MCM-48-supported norephedrine **2b** and prolinol **2c** were obtained by the same procedure with 0.50 mmol/g and 0.45 mmol/g, respectively.

2.4. General Procedure for the Asymmetric Addition of Diethylzinc to Aldehydes. To a stirred solution of MCM-48 silica **2** (5 mol%) in hexane (3 mL) was added Et_2Zn (3.0 mL, 1.0 M in hexane) at 0°C. The mixture was allowed to reach room temperature and then aldehyde (1.5 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 10 h and the reaction progress was observed by TLC analysis. After disappearance of the starting material, the reaction was quenched at 0°C by addition of saturated NH_4Cl solution. The catalyst was removed by filtration and washed with CH_2Cl_2. The filtrate was extracted with CH_2Cl_2, dried over Na_2SO_4, and filtered, and solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel with 10% AcOEt/hexane. The enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H column, 3% of 2-propanol in hexane, 0.5 mL/min, and detection at 254 nm). Racemic comparison samples were prepared by reactions of the corresponding aldehydes with EtMgBr. Configurations were assigned by comparison with known elution order from a chiral column.

2.5. General Procedure for the Ru-Catalyzed Asymmetric Transfer Hydrogenation to the Ketones with Immobilized Ligand **2b**. A suspension was formed by the mixture of $[RuCl_2(p\text{-cymene})]_2$ (5 mg, 0.008 mmol) and mesoporous silica-supported norephedrine **2b** (0.016 mmol) in 2-propanol (5 mL). The mixture was heated at 80°C for 30 min under nitrogen atmosphere. To this resulting solution, a degassed solution of ketone (0.83 mmol) with KOH (2.3 mg, 0.04 mmol) in 2-propanol (10 mL) was added and the mixture was stirred at room temperature for 3~4 h. The reaction was monitored by TLC analysis and after completion of the reaction it was neutralized with aqueous NH_4Cl solution (1 mL). The immobilized ligand **2b** was filtrated on a glass filter and washed with water and ethyl acetate. The obtained ligand was dried and used for the next reaction. The excess 2-propanol was removed under reduced pressure and diluted with water and ethyl acetate. The organic layer was washed with brine and dried over $MgSO_4$ and the crude product was purified by short-column chromatography (hexane-ethyl acetate 95/5 as eluent). Enantiomeric excess of the product was determined by HPLC analysis using Chiralcel OD-H column (3% of 2-propanol in hexane, 1 mL/min).

3. Results and Discussion

3.1. Preparation and Characterization of the MCM-48-Supported Chiral Amino Alcohols **2**. Soai and coworkers have reported asymmetric addition of diethylzinc reagent to aldehyde catalyzed by silica gel-supported ephedrine [41]. The immobilization of optically active (−)-ephedrine, (−)-norephedrine, and (−)-prolinol onto MCM-48 silica was easily performed through two steps as shown in Scheme 1. Treatment of MCM-48 silica with (3-chloropropyl)trimethoxysilane in refluxing toluene gave chloropropylated MCM-48 silica **1** with maximum loading of chloropropyl group (1.1 mmol/g $(CH_2)_3Cl$/g). Reaction of the modified MCM-48 silica **1** with an excess of (−)-ephedrine, (−)-norephedrine, and (−)-prolinol in refluxing toluene under basic condition afforded MCM-48-supported ephedrine **2a** (0.47 mmol/g), **2b** (0.50 mmol/g), and **2c** (0.45 mmol/g), respectively.



Scheme 1: Preparation of the MCM-48-supported chiral amino alcohols **2**.

Table 1: Structural characteristics of MCM-48-supported chiral amino alcohols **2**.

Sample	Surface area	Pore diameter	Pore volume	Loading amount
MCM-48	1250 m^2/g	3.15 nm	0.71 cm^3/g	—
2a	758 m^2/g	2.65 nm	0.50 cm^3/g	0.47 mmol/g
2b	767 m^2/g	2.72 nm	0.54 cm^3/g	0.50 mmol/g
2c	794 m^2/g	3.11 nm	0.61 cm^3/g	0.45 mmol/g

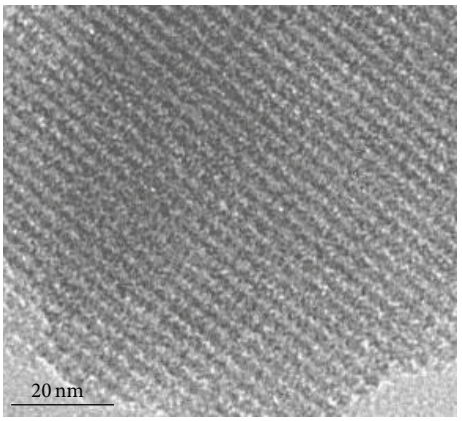


Figure 1: TEM image of MCM-48-supported amino alcohol **2a**.

The degrees of functionalization were determined by weight gain or elemental analysis. Some physical properties of the modified MCM-48 are summarized in Table 1. The data showed that the functionalized MCM-48 possesses characteristic pore structure of mesoporous material containing high specific surface area and high mesoporous volume. Surface area and pore diameter of MCM-48 **2** decreased due to the grafting of organic functional group. HRTEM image was obtained after the modification of the parent MCM-48

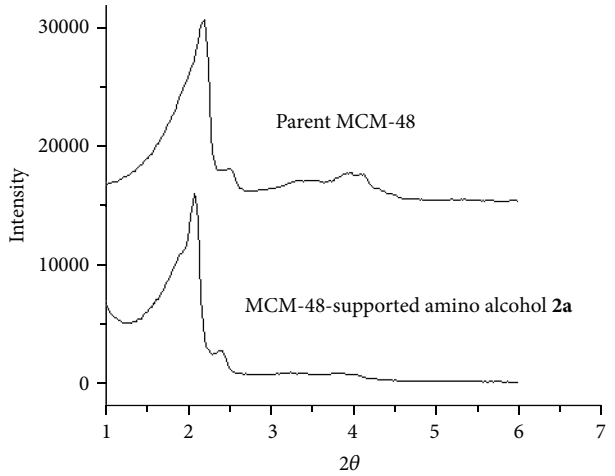
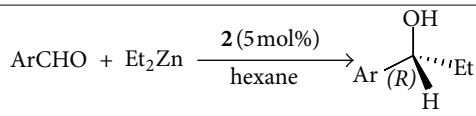


Figure 2: XRD pattern of MCM-48-supported amino alcohol **2a**.

silica shown in Figure 1. The 3D cubic structure and the pore arrays are conserved after the anchoring of chiral ligand onto MCM-48 silica, which is also confirmed by XRD in Figure 2. Apparently, there is no change of the lattice parameters upon the functionalization process.

3.2. Catalytic Enantioselective Addition of Diethylzinc to the Aldehyde. With the MCM-48-supported chiral amino alcohols **2** in hand, we examined their catalytic efficiency in the addition of diethylzinc to aldehydes in hexane. As shown in Table 2, satisfactory enantioselectivities and high yields were obtained in the presence of MCM-48-supported ephedrine **2a**. The results are compared with those obtained using previously reported silica gel-supported ephedrine (entries 5 and 7) [42]. MCM-48-supported ephedrine **2a** gave much higher reaction rate and better asymmetric induction than

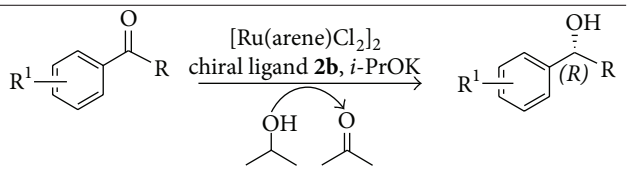
Table 2: Asymmetric addition of diethylzinc to aldehydes in the presence of **2**[a].



Entry	Ar	Ligand **2**	Yield (%)[b]	e.e. (%)[c]
1	Ph	**2a**	86	50
2[d]	Ph	**2a**	88	52
3	Ph	**2b**	75	7
4	Ph	**2c**	80	6
5[e]	Ph	Silica gel-supported **2a**	59	25
6	*o*-$MeOC_6H_4$	**2a**	90 (86)[f]	57 (54)[f]
7[e]	*o*-$MeOC_6H_4$	Silica gel-supported **2a**	65	34
8	*p*-MeC_6H_4	**2a**	82	43
9	*p*-ClC_6H_4	**2a**	90	50

[a]Reactions were carried out in hexane at room temperature using 2 equiv. of Et_2Zn unless otherwise noted. Absolute configuration was assigned by the elution order from chiral column. [b]Determined by GC analysis. [c]Determined by HPLC analysis using Chiralcel OD-H column (3% of 2-propanol in hexane, 0.5 mL/min). [d]10 mol% of ligand was used. [e]See [41]. [f]The catalyst was reused three times.

Table 3: Asymmetric transfer hydrogenation of ketones using immobilized ligands **2b**[a].



Entry	Ketone[b]	Time (h)	Conv. (%)[c]	e.e. (%)[d]
1	Acp	3	96 (92)[e]	77 (74)[e]
2	Pp	3	94	70
3	3-OMe-Acp	3	98	75
4	4-Cl-Acp	3	99	71
5[f]	4-Cl-Acp	4	92	82

[a]The reactions were carried out at room temperature in 2-propanol; ketone : Ru : ligand : KOH = 100 : 1 : 2 : 5. [b]Acp = acetophenone and Pp = propiophenone. [c]Determined by GC analysis. [d]Determined by HPLC analysis using Chiralcel OD-H column (3% of 2-propanol in hexane, 1 mL/min). [e]The catalyst was reused two times. [f]$[RuCl_2(hexamethylbenzene)]_2$ was used instead of $[RuCl_2(p\text{-cymene})]_2$.

silica gel-supported ephedrine **2a**. In the case of benzaldehyde, the enantioselectivity was greatly increased from 25% to 52% by the use of MCM-48 support (entry 2 versus 5). The improved outcome of the reaction seems to be attributed to crystalline structure of MCM-48 support. The MCM-48 framework allows an ordered array of chiral catalytic sites on the pore surface. The ordered array leads to elegant site-isolation, which may result in enhanced enantioselectivity. It is also noteworthy that our results are comparable to those of the homogeneous system using *N*-alkyl ephedrine [42]. Next, we did a recycling experiment using chiral ligand **2a**. We successfully recovered the catalyst and reused it twice without further addition of Ru-complex (entry 6). However, poor enantioselectivity was observed when the reaction was performed with MCM-48-supported ligands **2b** and **c** (entries 3 and 4).

3.3. Catalytic Asymmetric Transfer Hydrogenation of Ketones. Next, the efficiency of MCM-48-supported norephedrine **2b** was assessed in ruthenium-catalyzed asymmetric transfer hydrogenation of ketones. The chiral ruthenium catalyst was generated *in situ* by mixing $[Ru(\eta^6\text{-arene})Cl_2]_2$ and supported ligand **2b** (Ru : ligand = 1 : 2) in 2-propanol at 80°C for 30 min. The catalyst afforded (*R*)-secondary alcohols in up to 82% enantiomeric excess with 99% conversion. The reaction conditions and results are summarized in Table 3. $[Ru(hexamethylbenzene)Cl_2]_2$ as a Ru(II) source gave somewhat higher enantiomeric excess than $[Ru(p\text{-cymene})Cl_2]_2$. It should be noted that MCM-48-supported ligand **2b** could serve as an effective enantioselective chiral ligand [43].

4. Conclusions

The study successfully showed that mesoporous MCM-48 silica can be used as a potential inorganic support for the synthesis of heterogeneous catalysts for the asymmetric addition of diethylzinc reagent to aldehydes and asymmetric transfer hydrogenation of ketones. Promising results were obtained with MCM-48-supported ephedrine, in which ordered structure of MCM-48 had a positive effect on the conversation (99%) enantioselectivity (82%). The synthesis of other MCM-48-supported chiral ligands for the asymmetric catalysis is underway in our laboratory.

Conflict of Interests

All authors declare that they have agreed to publish this paper and that it does not have any contents with conflict of interests.

Acknowledgments

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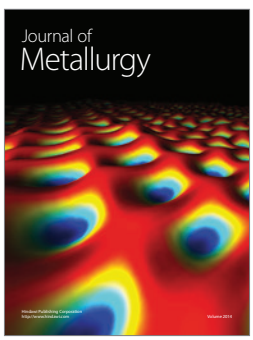
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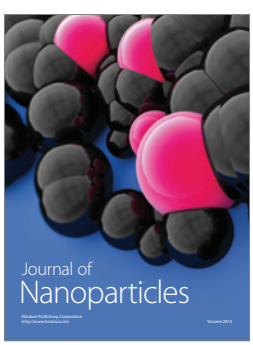
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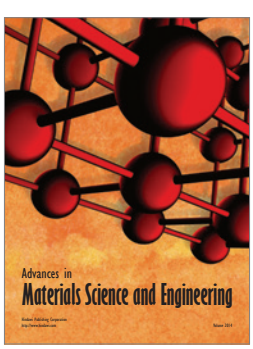
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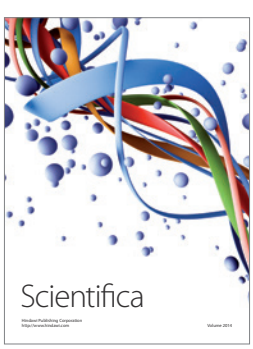
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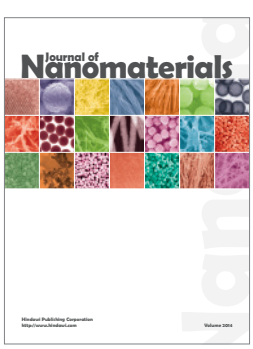
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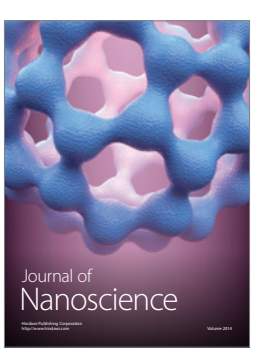
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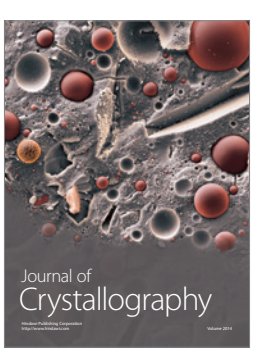
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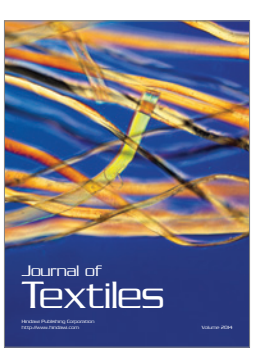
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