Research Article

Mesoporous Silica-Supported Sulfonyldiamine Ligand for Microwave-Assisted Transfer Hydrogenation

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N-Sulfonyl-1,2-diamine ligands, derived from 1,2-diaminocyclohexane and 1,2-diaminopropane, were immobilized onto mesoporous SBA-15 silica. The SBA-15-supported sulfonyldiamine-Ru complex was prepared *in situ* under microwave heating at 60 W for 3 min. The prepared sulfonyldiamine-Ru complex was used as an efficient catalyst for the transfer hydrogenation of ketones to the corresponding secondary alcohols. The heterogeneous complex showed extremely high catalytic activity with 99% conversion rate under microwave heating condition. The complexes were regenerated by simple filtration and reused two times without significant loss of activity.

1. Introduction

Catalytic transfer hydrogenation of ketones and imines is an attractive method for the preparation of alcohols or amines [1–3]. Several homogeneous catalysts have been proposed for the transfer hydrogenation reactions [4–10]. However, the separation and recycling of homogeneous catalysts are complicated. Therefore, attempts were made to attach the catalyst to an insoluble support to improve the handling and separation of catalyst from the reaction mixture and also its recycling [11–13]. Several homogeneous catalysts were immobilized on supports such as dendritic polymers [14–16], silica [17], polystyrene [18, 19], biphasic catalysis [20], and Al-SBA-15 materials [21]. However, despite having highly ordered mesoporous structures with uniform pore diameter (6~7 nm) and high surface area, very few catalysts were tested on silica SBA-15 matrix [22–24].

Due to well-known silicon chemistry, various organic groups could be robustly anchored in the surface of SBA-15 silica. This strategy would offer practical advantages such as simplified separation, easy recovery, and poten-tial reuse of catalyst over traditional solution-phase chemistry [25]. Our interest in recyclable immobilized catalysts led us to prepare mesoporous SBA-15-supported N-sulfonyl-1,2-diaminocyclohexane and 1,2-diaminopro-pane ligands and their Ru complexes for transfer hydrogenation reaction. Since heterogeneous catalysis typically requires long reaction time, we used here microwave-assisted reactions which occur much faster than conventional heating reactions [26–28]. To the best of our knowledge, we described here SBA-15-supported N-sulfonyl-1,2-diaminocyclohexane and 1,2-diaminopropane ligands and their Ru complexes for the heterogeneous transfer hydrogenation of ketones under microwave irradiation conditions for the first time.

2. Experimental

2.1. Preparation of the Mesoporous SBA-15 Silica. Mesoporous silica SBA-15 was synthesized according to Zhao et al. [24]. Briefly, 4 g of Pluronic P123 was dissolved in 30 g of water and 120 g of 2 M HCl solution at room temperature under

vigorous stirring. Then 8.5 g of TEOS was added into that solution under stirring. The reaction mixture was maintained at room temperature for 10–12 h and then at 60°C for 48 h and then kept at 120°C for 24 h under static conditions in a Teflon-lined autoclave to generate materials with uniform pore diameter from 4 to 10 nm. The solid product was recovered and washed with DI water.

2.2. Preparation of the Trimethoxysilated N-Sulfonyl-1,2-diamines 2. To a solution of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (400 mg, 1.23 mmoL) in CH_2Cl_2 (10 mL) was slowly added a solution of 1,2-diaminocyclohexane **1a** (140 mg, 1.23 mmoL) and triethylamine (124 mg, 1.23 mmoL) in CH_2Cl_2 (7 mL) at −10°C. The reaction mixture was allowed to warm at room temperature and stirred for 2 h. The mixture was diluted with CH_2Cl_2 and washed with cold water. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography to give trimethoxysilylated *N*-sulfonyl-1,2-diaminocyclohexane **2a** in 85% yield. Compound **2b** was similarly prepared from 1,2-diaminopropane **1b** in 78% yield.

2.3. Preparation of the SBA-15-Supported Sulfonyldiamines 3. SBA-15 silica (1.0 g) was added to a solution of compound **2a** (110 mg, 0.27 mmoL) in toluene (15 mL) and the mixture was refluxed for 18 h. After filtration, the powder was washed several times with methylene chloride and dried under vacuum at 70°C to give SBA-15-supported *N*-sulfonyldiamine **3a**. Weight gain showed that 0.18 mmoL/g of compound **2a** was grafted in 1.0 g of SBA-15-silica **3a**. The SBA-15-supported *N*-sulfonyldiamine **3b** was also prepared from compound **2b** by the same procedure. Weight gain showed that 0.15 mmoL/g of compound **2b** was anchored in 1.0 g of the SBA-15 silica **3b**.

2.4. Characterization of the SBA-15-Supported Ligand 3. Mesostructures of the synthesized materials were identified by powder X-ray diffractions (XRD). The XRD patterns were obtained by using a Rigaku Multiflex diffractometer with a monochromated high-intensity CuK_α radiation ($\lambda = 1.54$ Å). Scanning was performed under ambient conditions over the 2θ region of 0.6–4.5° at the rate of 0.1°/min (20 kV, 10 mA). The XRD diffractograms showed three peaks at 100, 110, and 200 which revealed that the synthesized structure was cubic *Im3m*. The transmission electron microscopy (TEM) was performed with a FEI Tecnai G^2 microscope operated at 200 kV. The TEM sample was prepared by placing a few drops of SBA-15 powder dispersed in ethanol on a carbon grid and allowed to dry for 5 min before TEM analysis. Some of the samples, which have big 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-15 was degassed at 300°C for 9 h before 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, and 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.

2.5. Transfer Hydrogenation of Ketones under Microwave Irradiation. SBA-15-supported ligand **3** (0.03 mmoL) was suspended in water (2 mL) and heated with [Ru(*p*-cymene)Cl_2]$_2$ (6.12 mg, 0.01 mmoL) for 3 min under MW (60 W). Ketone (1 mmoL) and HCO_2Na (340 mg, 5 mmoL) were added to the solution and heated under MW (40~60 W) for short reaction time (Table 2) and the conversion was monitored by GC analysis. After completion of the reaction (GC analysis), the mixture was cooled at room temperature and diluted with diethyl ether. The organic layer was washed by brine and dried over $MgSO_4$. The crude product was purified by short column chromatography.

3. Results and Discussion

Preparation of the SBA-15-supported *N*-sulfonyldiamine **3a** and *N*-sulfonyldiamine **3b** was performed in a two-step reaction shown in Scheme 1. Reaction of 1,2-diaminocyclohexane with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane produced trimethylsilylated *N*-sulfonyl-1,2-diaminocyclohexane **2a** with a yield of 85%. Subsequent condensation of **2a** with the surface silanols of SBA-15 silica support in refluxing toluene yielded immobilized *N*-sulfonyldiamine SBA-15 silica **3a** (loading ratio: 0.18 mmoL/g).

Similarly, immobilized *N*-sulfonyldiamine **3b** (loading ratio: 0.15 mmoL/g) was obtained from 1,2-diaminopropane. The loading ratios for the SBA-15-supported *N*-sulfonyldiamines were determined by measuring weight gain. The TEM images are obtained after the modification of the parent SBA-15 silica which showed that the hexagonal symmetry of the pore arrays is conserved after immobilization of organic moiety onto the SBA-15 silica (Figure 1). The hexagonal symmetry of the pore arrays also appeared in XRD analysis (Figure 2).
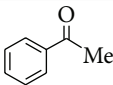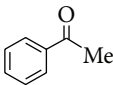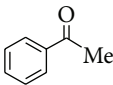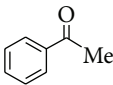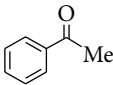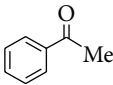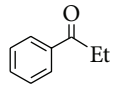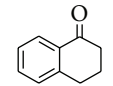
The BET surface area and pore diameter of the SBA-15 silica were measured before and after immobilizing the ligand (Table 1 and Figure 3). It was clearly observed that both the surface area and pore diameter were significantly decreased following the modifications.

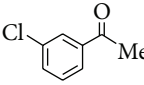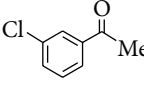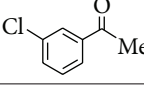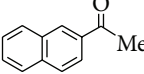The SBA-15-supported Ru(II) complexes were prepared *in situ* by MW-assisted heating of a mixture of [Ru(*p*-cymene)Cl_2]$_2$ and the supported ligand **3** in H_2O at 1 : 3 ratio. With the SBA-15-supported *N*-sulfonyldiamine ligand **3a**, we first performed microwave-assisted transfer hydrogenation of acetophenone (1 mmoL) as a model substrate using [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmoL) and 0.03 mmoL of ligand **3a** in aqueous HCO_2Na under 80 W microwave irradiation. The catalyst showed high activity and provided corresponding alcohol in a quantitative yield within 30 min reaction time (Table 2, entry 1). Surprisingly, the catalyst showed outstanding catalytic activity to give the corresponding alcohol when the microwave power decreased to 60 W (entries 2,

TABLE 1: Structural information of the SBA-15-supported sulfonyldiamine **3**.

Sample	Surface area	Pore diameter	Pore volume	Functional group
SBA-15	750 m^2/g	8.33 nm	0.83 cm^3/g	—
3a	481 m^2/g	7.25 nm	0.39 cm^3/g	0.18 mmoL/g
3b	504 m^2/g	7.51 nm	0.45 cm^3/g	0.15 mmoL/g

TABLE 2: Microwave-assisted transfer hydrogenation in the presence of **3**[a].

$$R' \overset{O}{\underset{}{\bigcirc}} R \xrightarrow[\text{HCO}_2\text{Na-H}_2\text{O, MW}]{\textbf{3} + [\text{Ru}(p\text{-cymene})\text{Cl}_2]_2} R' \overset{OH}{\underset{}{\bigcirc}} R$$

Entry	Ketone	Ligand	Power (W)	Time (min)	Conv. (%)[b]
1	phenyl C(=O)Me	**3a**	80	30	100
2	phenyl C(=O)Me	**3a**	60	30	99 (94)[c]
3	phenyl C(=O)Me	**3a**	60	30	95[d]
4	phenyl C(=O)Me	**3a**	50	30	96 (92)[c]
5	phenyl C(=O)Me	**3a**	40	40	93
6	phenyl C(=O)Me	**3b**	60	40	90
7	phenyl C(=O)Et	**3a**	60	40	93 (88)[c]
8	1-tetralone	**3a**	60	40	90
9	Cl-phenyl C(=O)Me	**3a**	60	25	100
10	Cl-phenyl C(=O)Me	**3b**	60	30	98 (95)[c]
11	Cl-phenyl C(=O)Me	**3a**	40	30	95
12	naphthyl C(=O)Me	**3a**	60	35	98

[a]Molar ratio; ketone : Ru : ligand **3** (loading ratio = 0.18 and 0.15 mmoL/g) = (100 : 1 : 3), HCO$_2$Na (5 equiv.). [b]Determined by GC analysis. [c]Isolated yield. [d]After third use of the catalyst (according to entry 2).
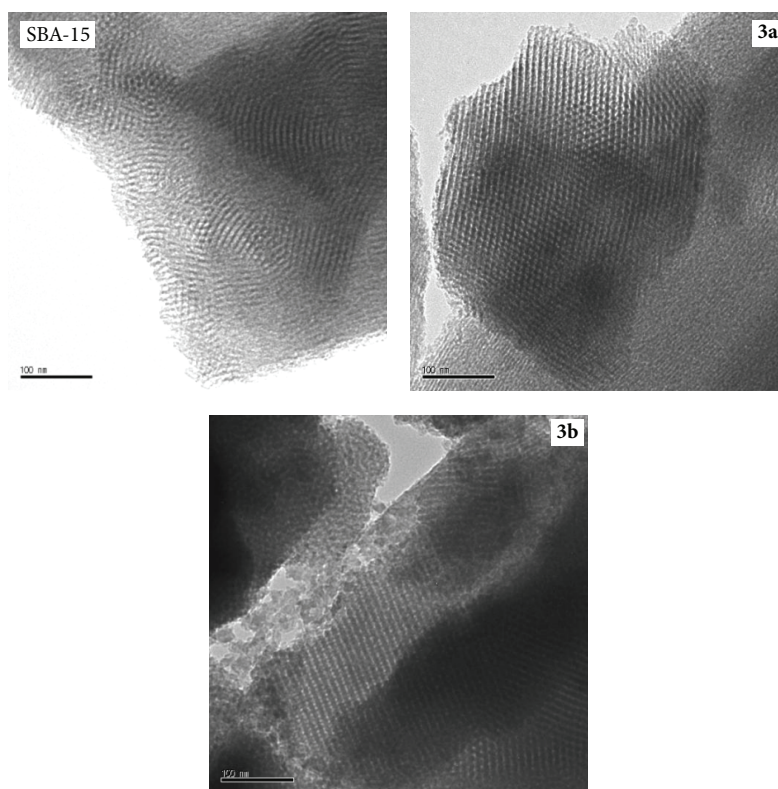
FIGURE 1: TEM images of parent SBA-15- and SBA-15-supported ligands **3a** and **3b**.
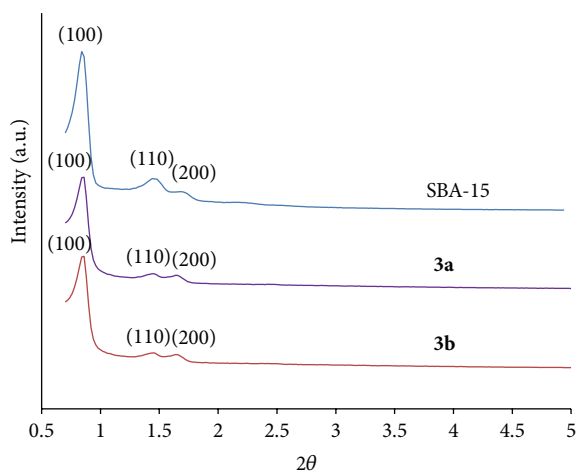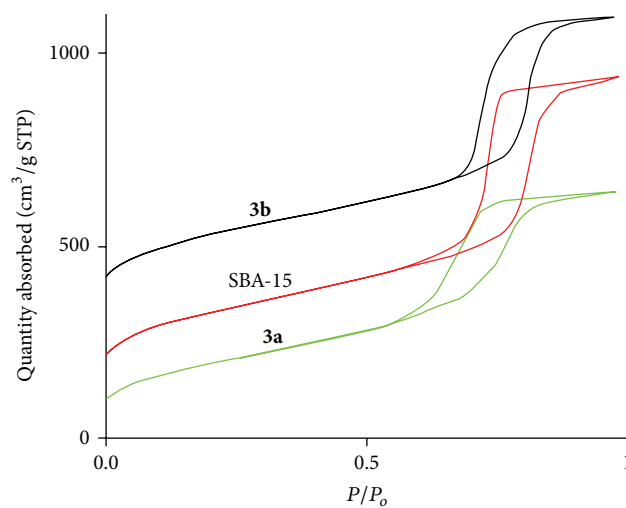

FIGURE 2: XRD pattern of modified SBA-15.

FIGURE 3: Nitrogen adsorption-desorption isotherms.

3). When the MW power was further decreased to 50–40 W, the conversion was also decreased (entries 4, 5). The propiophenone and α-tetralone were smoothly converted into the corresponding alcohol with excellent yield (entries 7, 8).

Recently, Baruwati et al. [31] reported magnetically recoverable supported ruthenium catalyzed transfer hydrogenation of carbonyl compounds in isopropanol at 100°C under microwave irradiation conditions. In this study, we performed hydrogen transfer reaction in pure water under

mild reaction condition, which is safer, more economical, more convenient, and greener for industrial applications.

Finally, we examined the transfer hydrogen reaction of 3-chloroacetophenone and 2-acetylnaphthalene substrates and excellent results were obtained under the same microwave irradiation conditions (entries 9–12). The MW-assisted reaction reached completion with quantitative conversion within
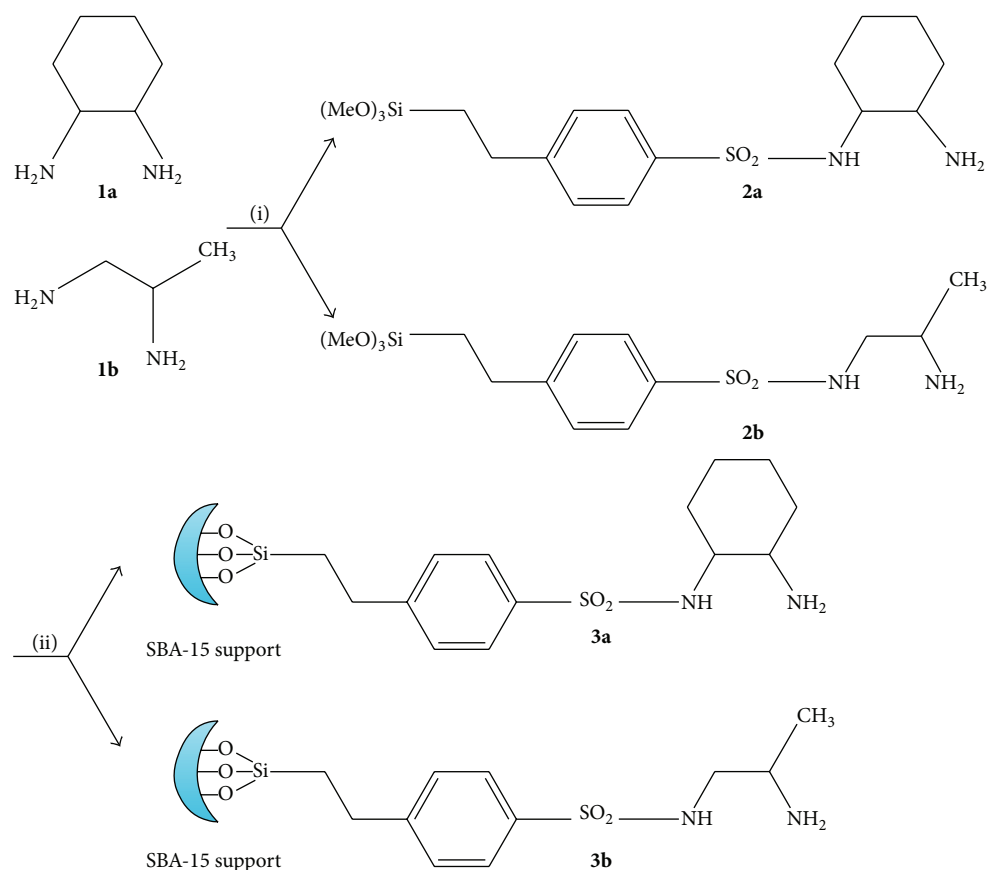
Scheme 1: Preparation of the SBA-15-supported *N*-sulfonyldiamine **3**. (i) 2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane, triethylamine, CH_2Cl_2 −10°C to room temperature, 2 h; (ii) SBA-15, toluene, 105°C, 18 h.

25 min with a TOF of up to $245\,h^{-1}$ in presence of SBA-15-supported ligand **3a** (entry 9). The conversions seemed to be insensitive to substituent or structure of the substrates. It is noteworthy that the Ru catalyst could be reused with consistent catalytic activity (entry 3). The SBA-15-supported ligand **3b** also showed similar catalytic activity to ligand **3a** under similar reaction conditions (entries 6, 10).

4. Conclusion

We have prepared recyclable SBA-15-supported *N*-sulfonyl-1,2-diamine ligands from 1,2-diaminocyclohexane and 1,2-diaminopropane. Microwave-assisted heating was employed for heterogeneous Ru-catalyzed transfer hydrogenation of ketones. The immobilized *N*-sulfonyldiamine Ru-complex showed extremely high catalytic activity (TOF $245\,h^{-1}$) under microwave heating condition. Moreover, the catalyst could be reused without significant loss of activity.

Conflict of Interests

All authors declare that this paper does not have any content with conflict of interests.

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