Facile synthesis of a mesoporous silica-supported catalyst for Ru-catalyzed transfer hydrogenation of ketones†

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A convenient method for preparation of a mesoporous silica-supported chiral catalyst by postgrafting a homogeneous catalyst on SBA-15 was developed and its application in the asymmetric transfer hydrogenation of aromatic ketones was investigated.

The immobilization of homogeneous chiral catalysts for asymmetric reactions is a powerful method for the synthesis of optically active molecules and has attracted a great deal of interest due to the potential features of easy separation and efficient recycling, as well as minimal product contamination from metal leaching.[1] Recently, many practical approaches[2] have been introduced to immobilize homogeneous chiral catalysts onto supports through covalent methods. Especially, the covalent immobilization on mesoporous materials has exhibited some salient features.[3] These mesoporous silica-supported chiral catalysts have regular and adjustable pores that do not allow the aggregation of active catalysts and can keep excellent stereocontrol performance. Furthermore, they are easy and reliable to reuse *via* simple nanofiltration. Besides, they also have a facile preparation, remarkable thermal and mechanical stability, and high density of catalytically active units because of the high surface area. Due to these advantages, the immobilization of homogeneous catalysts on mesoporous materials represents a rapidly growing field that is on the verge of being applied in industry. Recently, some of mesoporous materials, such as MCM-41 (ordered hexagonal),[4] MCM-48 (ordered cubic)[5] and SBA-15 (ordered hexagonal),[6] have been used successfully as the supports to immobilize homogeneous chiral catalysts.

Optically active 1,2-diphenylethylenediamine [(*R*,*R*)-DPEN] is a highly effective chiral ligand for the transfer hydrogenation of ketones.[7] The immobilization of its derivatives [(*R*,*R*)-TsDPEN] onto mesoporous materials[8] has also been explored. However, apart from the tedious synthetic process, these MCM-41 or SBA-15-supported chiral catalysts still afforded worse recycling than that of those immobilized on silica gel. Moreover, detailed discussion of their differences, especially the structures of MCM-41 or SBA-15-supported chiral catalysts, is unavailable.

Recently, we reported a series of mesoporous catalysts,[9] especially Ru-SBA-15,[9a–b] and their application in catalytic processes. As an extension of our previous study, we herein develop a convenient and rapid method for the preparation of mesoporous silica-supported chiral catalyst **6** by the postgrafting method based on mesoporous materials (SBA-15), and apply it in the Ru-catalyzed asymmetric transfer hydrogenation of aromatic ketones. Our attention focuses on the construction of highly ordered mesoporous silica-supported chiral catalysts and investigation of different stereocontrol performances through comparison of catalyst **6** with catalyst **5**, prepared by the postmodification method based on mesoporous materials (Ru-SBA-15).

The mesoporous silica-supported chiral catalyst, abbreviated as Ru-SBA-15/(*R*,*R*)-DPEN (**6**), was prepared by the postgrafting method. As shown in Scheme 1, catalyst **6** was obtained from the reaction of the commercially available (trisethoxysilyl)ethyldiphenylphosphine of (*R*,*R*)-DPEN in dry CH_2Cl_2 for 5 h at room temperature, followed by anchoring onto SBA-15 through refluxing in toluene for 24 h. IR (KBr): 3450, 2960, 2920, 2870, 1650, 1440, 1050, 959, 806, 692, 545, 468 cm^{-1}; ^{29}Si MAS-NMR (79.5 MHz): −116, −106, −97 ppm; ^{13}C CP-MAS (100.6 MHz): 129, 72, 63, 22 ppm; ^{31}P CP-MAS (169.3 MHz): 71 ppm; elemental analysis (%): C 3.39, H 2.55, N 0.19. For comparison, catalyst **5** was also synthesized by the postmodification of (*R*,*R*)-DPEN onto Ru-SBA-15[9a–b] with a similar strategy. The inductively coupled plasma (ICP) optical emission spectrometer analyses showed that the Ru-loading amounts in catalysts **5** and **6** were 6.80 and 6.26 mg per gram of catalyst. The pore sizes of catalysts **5** and **6** were measured to be 4.8 and 6.3 nm, as shown in Table 1 in Fig. 1.

The powder XRD patterns revealed that catalysts **5** and **6** showed one similar intense peak and two weak peaks indicative of (100), (110), and (200) reflections in Fig. 1, suggesting that the hexagonal arrayed pore structure (*p*6*mm*) could be preserved after modification and postgrafting.[10] The decrease in the peak intensity implied that the modification or postgrafting might disturb the ordered mesoporous structure to a certain degree. The TEM morphologies further confirmed that both catalysts displayed a two-dimensional hexagonal arrangement of one-dimensional channels with uniform size (Fig. 2). N_2 adsorption–desorption isotherms in Fig. 3 revealed that both catalysts exhibited the typical IV type isotherms with a steep increase in adsorption at P/P_0 = 0.40–0.70. On the basis of the N_2 adsorption–desorption isotherms, some structural parameters were calculated and listed in Table 1, which is inserted in Fig. 1. It is found that the catalysts by the modification or postgrafting method resulted in a decrease in the nanopore size, surface area, and pore volume (sample **5** *versus* **3**, and sample **6** *versus* SBA-15). This could be attributed to the coverage by the ruthenium complexes on the channel surfaces of the Ru-SBA-15 or SBA-15, resulting in an increase in the wall thickness.[9a–b]

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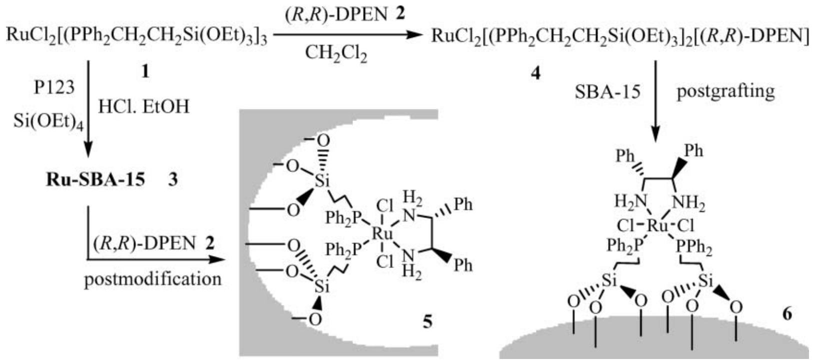

Scheme 1 Syntheses of immobilized catalysts **5** and **6**.

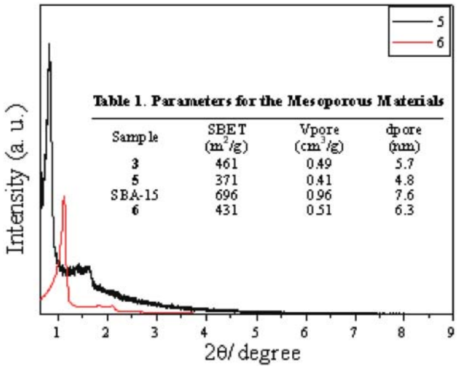

Table 1. Parameters for the Mesoporous Materials

Sample	SBET (m^2/g)	Vpore (cm^3/g)	dpore (nm)
3	461	0.49	5.7
5	371	0.41	4.8
SBA-15	696	0.96	7.6
6	431	0.51	6.3

Fig. 1 The powder XRD patterns of the mesoporous silica-supported chiral catalysts **5** and **6**.

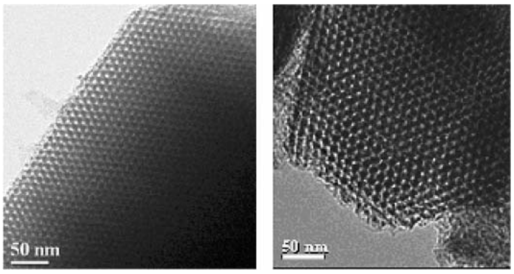

Fig. 2 The TEM images of the catalysts **5** and **6** viewed along [100] directions.

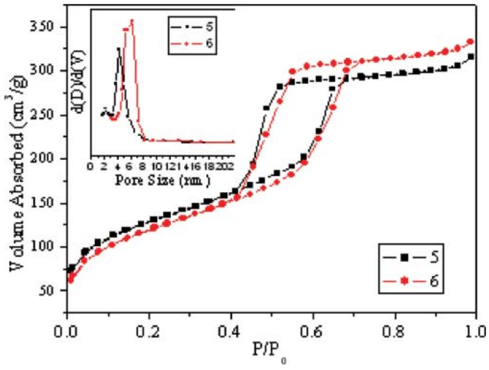

Fig. 3 Nitrogen adsorption–desorption isotherms of the mesoporous silica-supported chiral catalysts **5** and **6**.

The asymmetric transfer hydrogenation of ketones was carried out according to the reported method.[7] Generally, catalyst **6** was found to be highly effective in the asymmetric transfer hydrogenation of aromatic ketones. The preliminary results are summarized in Table 2. Taking the acetophenones as an example, the asymmetric transfer hydrogenation provided (*R*)-1-phenyl-1-ethanol in more than 99% yield and 99.5% ee (entry 1), which is higher than that obtained with the parent, molecular catalyst, [$RuCl_2(PPh_3)_2$(*R*,*R*)-DPEN)].[7f–7g] Besides, catalyst **6** also gave values of more than 98% ee using 1-acetonaphthone and substituted acetophenones as substrates (entries 2–5). Of particular note is that the reaction can be run at a much higher S : C ratio without obviously affecting the ee value, as exemplified by the hydrogenation of **8** at S/C = 500 (entry 6).

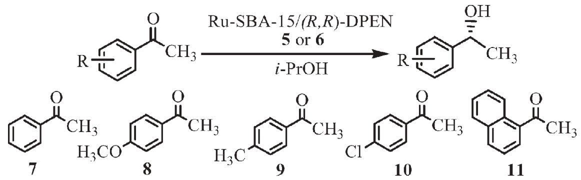

Table 2 Asymmetric transfer hydrogenation of aromatic ketones[a]

Entry	Substrate	Catalyst	Run	Conv. (%)[b]	Ee (%)[b]
1	**7**	**6**	1	>99	99.5
2	**8**	**6**	1	>99	99.9
3	**9**	**6**	1	>99	98.4
4	**10**	**6**	1	>99	99.1
5	**11**	**6**	1	>99	99.8
6	**8**	**6**	1	>99	97.2[c]
7	**7**	**5**	1	81.9	59.1
8	**7**	**2** + **3**	1	17.9	79.3
9	**8**	**6**	2	>99	99.8[d]
10	**8**	**6**	3	>99	99.6[d]
11	**8**	**6**	4	>99	99.2[d]
12	**8**	**6**	5	>99	99.5[d]
13	**8**	**6**	6	>99	99.4[d]
14	**8**	**6**	7	>99	98.4[d]
15	**8**	**6**	8	>99	93.6[d]

[a] Reactions were carried out in CH_2Cl_2. Reaction conditions: catalyst (5.03 μmol of Ru), *i*-PrOH (0.013 mol), *i*-PrOK (0.1 mol), ketone (0.5 mmol), reaction temperature (50 °C), reaction time (24–48 h), argon atmosphere. [b] Determined from chiral GC analysis. The absolute configuration of the product is *R*. [c] Data were obtained at S/C = 500. [d] Recovered catalysts were used.

In order to further compare the catalytic performances, two control experiments were also carried out using **5** and the 1 : 1 (mole ratio) mixture of Ru-SBA-15 and (*R*,*R*)-DPEN as catalysts under similar reaction conditions. It was found that **5** afforded the corresponding alcohol in 81.9% conversion and 59.1% ee, while the 1 : 1 (mole ratio) mixture of Ru-SBA-15 and (*R*,*R*)-DPEN gave the corresponding alcohol in only 17.9% conversion and 79.3% ee (entries 7 and 8). As compared with catalyst **6**, the low enantioselective activity of **5** may be due to the fact that the postmodified organic groups [(*R*,*R*)-DPEN] are mainly near the pore mouth because of mass transfer,[11] while distributing (*R*,*R*)-DPEN ligand onto Ru-SBA-15 randomly might result in the jam or disorder of nanopores. All these observations indicate that there are difficulties in forming effective coordination to Ru due to the Ru in the nanopores. A similar phenomenon is also observed by Li *et al.*[6]

Therefore, when comparing catalyst **5** and Tu's catalyst[8] with catalyst **6**, the following two factors could be taken into consideration. Firstly, the Ru loadings of catalyst **6** occur during formation of the homogeneous catalysts that are anchored on SBA-15 *via* covalent immobilization, while the Ru loadings of Tu's catalyst occur at the *in situ* complexing process and the presence of some nonvalent adsorption is unavoidable. Hence catalyst **6** avoids further loss of Ru after forming the mesoporous catalyst. ICP analysis after the eighth recycling experiment process further confirms the result that the loss of Ru could be neglected (6.22 *versus* 6.26 mg per gram of catalyst). This also explains why the catalytic activity of Tu's catalyst decreases abruptly after three recycling experiments, due to an amount of loss of Ru. Secondly, because the homogeneous catalysts were immobilized on the external surface of the support in catalyst **6**, it is easy to form a regularly dispersive arrangement of the catalytic species. This kind of arrangement not only offers reasonable space for chiral recognition of the substrate, but also restricts the aggregation or disorder of the catalytic species, resulting in higher *ee* values. On the contrary, the homogeneous catalysts were immobilized on the internal surface of the support in the catalyst **5**.[11] The jam or disorder of the catalyst in the nanopores is a key factor to decrease the enantioselectivity. An important feature of the design of catalyst **6** is the easy and reliable separation *via* simple filtration. For example, upon completion of the reaction, catalyst **6** was quantitatively recovered *via* filtration. In eight consecutive reactions, the catalyst afforded more than 99% conversions and high ee values with a slight decrease in the eighth recycling experiment (93.6%). This kind of phenomenon confirms the advantages of Ru-loading prior to the formation of the heterogeneous catalyst.

In conclusion, we report the facile preparation of a mesoporous silica-supported chiral catalyst **6** by postgrafting, in which **6** was obtained by anchoring **4** onto SBA-15 through refluxing in toluene for 24 h. This kind of heterogeneous catalyst showed high catalytic activities (more than 99% yields for all tested ketones) and excellent enantioselectivities (more than 98% ee) for the asymmetric transfer hydrogenation of various aromatic ketones. Besides, catalyst **6** could be readily recovered and reused in multiple consecutive catalytic runs (up to 8 uses without unloading of Ru) with maintained high enantioselectivity, which is beneficial for possible industrial applications.

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