Microwave-assisted catalytic allylation of aldehydes promoted by a mesoporous silica-supported BINOL ligand in solid media†

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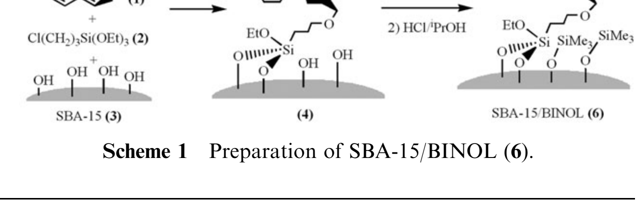
An efficient and operationally simple method for catalytic allylation has been developed and its application in the microwave-assisted catalytic allylation of aldehydes in solid media was investigated.

The development of allylation under catalysis has attracted a great deal of interest due to its extensive application in organic chemistry.[1] One of most successfully studied Lewis acid-catalyzed allylation reactions employs titanium complexes of 1,1-binaphthalene-2,2-diol (BINOL), with Ti(IV) Lewis acids as catalysts.[2] Although these catalysts show high catalytic activities and selectivities for allylation of aldehydes, their practical applications in industrial process are hindered due to long reaction time and difficulty in recovery and reuse of expensive titanium complexes. Microwave-assisted catalysis as a convenient method[3] can accelerate transition-metal-catalyzed reactions from hours or days to minutes, while immobilization[4] is well-known to solve the problem of transition-metal catalyst recycling. Furthermore, "solvent-free" catalytic processes can be regarded as green processes.[5] Thus, development of immobilization of homogeneous catalysts in microwave-assisted catalysis under solvent-free condition is a promising avenue in industry. Especially, in such a catalytic allylation reaction with Ti(IV) Lewis acid as a catalyst, addition of molecular sieves in the BINOL/Ti(IV) system is found to be extremely important for high reactivity and selectivity.[2a,b] Thus, searching for suitable analogues or substitutes for molecular sieves as supports is important in such catalytic allylation reactions. Mesoporous materials possessing the functions of molecular sieves have showed some salient features,[6] such as regular and adjustable pores, high surface area, remarkable thermal and mechanical stability and so on. These features demonstrate that mesoporous materials may be potentially ideal catalyst supports. Thus, a practical approach through immobilizing BINOL ligand onto mesoporous materials[7] for microwave-assisted catalysis in solvent-free system may combine these advantages in this allylation reaction. Although some mesoporous materials,[8] such as MCM-41 and SBA-15, have been successfully used as supports to immobilize homogeneous ligands or catalysts and some of them have exhibited high catalytic activities, the effectiveness of microwave-assisted catalysis employing mesoporous silica-supported BINOL ligand or catalysts for catalytic allylation of aldehydes in solid media has not yet been reported.

Recently, we reported a series of mesoporous catalysts and their applications in green catalytic processes.[9] We herein develop a facile preparation of mesoporous silica-supported ligand **6** by a post-grafting method based on SBA-15, and apply this to microwave-assisted Ti-catalyzed allylation of aromatic aldehydes in solid media. The research focuses on the following: (1) construction of highly ordered mesoporous silica-supported BINOL ligand; (2) investigation of different catalytic performances through a comparison of ligand **6** with the parent ligand BINOL; (3) exploration of its potential application in industry.

The mesoporous silica-supported BINOL ligand, abbreviated as SBA-15/BINOL (**6**), was prepared by a post-grafting method. As shown in Scheme 1, the mesoporous material **4** was synthesized by the reaction of $ClCH_2CH_2CH_2Si(OEt)_3$ **2** with **1**[10] followed by anchoring onto SBA-15 (**3**). The silicon-hydroxyl groups of **4** were then protected with HMDS groups.[7a] Finally, **6** was obtained successfully *via* removal of MOM protecting groups of hydroxyl groups at the binaphthyl backbone by using HCl/^{i}PrOH as deprotecting reagents. The ^{29}Si CP/MAS NMR measurement (Fig. 1(a)) showed clearly that **6** presented a strong Q^4 (−113 ppm), a medium T^3 (−71 ppm) and a weak T^2 (−63 ppm) peak in its spectrum. These values can be compared with typical isomer shift values of −48.5, −58.5 and −67.5 ppm for $T^1/T^2/T^3$ peaks ($T^3\{RSi(OSi)_3\}$, $T^2\{R(HO)Si(OSi)_2\}$, $T^1\{R(HO)_2SiOSi\}$), and −91.5, −101.5, −110 ppm for $Q^2/Q^3/Q^4$ signals ($Q^4\{Si(OSi)_4\}$, $Q^3\{(HO)Si(OSi)_3\}$, $Q^2\{(HO)_2Si(OSi)_2\}$).[11] The strong Q^4 peak suggested that **6** possessed mainly a network structure of $\{Si(OSi)_4\}$ and the relatively weak T^2 and T^3 peaks indicated the formation of $\{R(HO)Si(OSi)_2\}$ and $RSi(OSi)_3\}$ (R = organic ligand) as a part of wall in a mesoporous structure. The ^{13}C CP/MAS NMR spectrum displayed peaks around 128.7 ppm for benzene rings, and 0.1, 10.0, 26.3, 45.6 and 50.5 ppm for the other atoms, which were marked in Fig. 1(b). All these observations confirmed the successful post-grafting of ligands onto the mesoporous support. The amount of grafted



Scheme 1 Preparation of SBA-15/BINOL (**6**).

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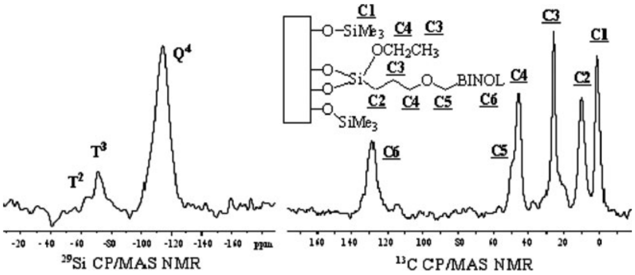
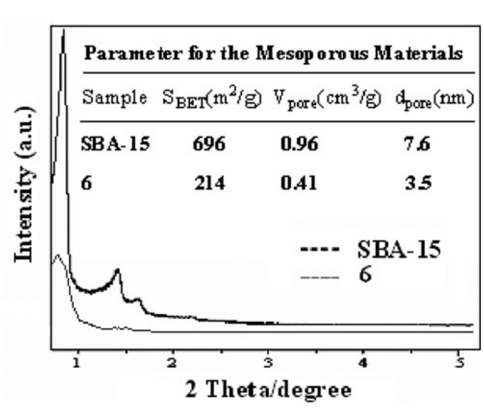


Fig. 1 The ^{29}Si CP/MAS NMR (**1a**) and ^{13}C CP/MAS NMR (**1b**) of **6**.

BINOL was found to be 24.5 mg/100 mg of solid support calculated from elemental analysis and thermal gravimetric data. The pore sizes of SBA-15 (**3**) and SBA-15/BINOL (**6**) were measured to be 7.6 and 3.5 nm.

The powder XRD patterns (Fig. 2) revealed that SBA-15/BINOL (**6**) showed one intense peak and two very weak peaks indicative of (100), (110) and (200) reflections, suggesting that the dimensional-hexagonal pore structure (*p*6*mm*) could be preserved after the post-grafting.[12] The reduced peak intensity in **6** indicated that the incorporation of the organic ligands onto the SBA-15 might disturb the ordered dimensional-hexagonal mesostructure by a certain degree. The TEM morphology further confirmed that **6** had a well-ordered mesostructure with the dimensional-hexagonal arrangement as shown in Fig. 3. From the structural parameters listed in Fig. 2, it was found that **6** obtained by a post-grafting method resulted in a decrease of nanopore size, surface area, and pore volume of **6** relative to SBA-15. This could be attributed to occupation of the ligands in the pore channels to make the pores narrower and coverage of the ligands on the channel surface resulting in an increase of the wall thickness.[9a–d]

The catalytic allylations of aromatic aldehydes under microwave irradiation in solid media were carried out through employing only a small excess of tetraallyltin as nucleophilic reagent based on consideration of green chemistry. This was not only useful to afford almost pure allylated products, but also prevented pollution from large amounts of hydrolyzed inorganic tin compounds during the work-up stage. As can be seen from Table 1, a variety of aromatic aldehydes **7a–11a** were cleanly reacted with 0.28 equiv. of tetraallyltin to give the corresponding homoallylic alcohols **7b–11b** in excellent yields, with a small amount of by-products **7c–11c** produced *via* the Meerwein–Ponndorf–Verley–Oppenauer process.[13] For example, combining benzaldehyde with tetraallyltin and 10 mol% of catalyst provided 1-phenyl-3-buten-l-ol in more than 99% conversion and 99.4% selectivity (entry 2), which was the nearly same as that obtained using the parent BINOL ligand (entry 1). Additionally, both reactions could be completed in a short reaction time (15 min), much faster than that without titanium(IV) isopropoxide (entry 3), or even than those using isopropanol and water as solvents in 12 h (entries 4 and 5). Of particular note was that the reaction could be run at 5% mol of catalysts without obviously affecting the selectivity, as exemplified by the allylation of **7a** (entry 6).


Parameter for the Mesoporous Materials

Sample	S_{BET}(m^2/g)	V_{pore}(cm^3/g)	d_{pore}(nm)
SBA-15	696	0.96	7.6
6	214	0.41	3.5

Fig. 2 Powder XRD patterns of SBA-15 and **6**.

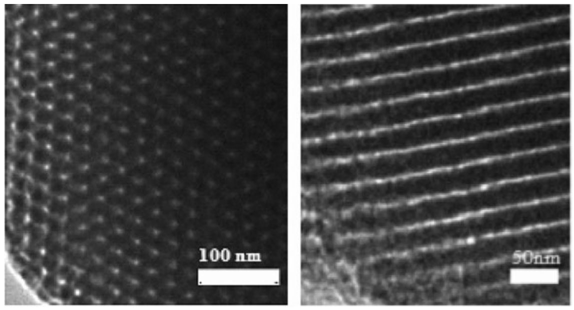
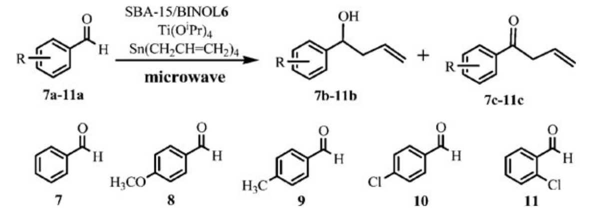


Fig. 3 TEM images of **6** viewed along [100] and [001] directions.

Table 1 Microwave-assisted catalytic allylation of aromatic aldehydes[a]



Entry	Substrate	Ligand	Run	Conv.[b] (%)	Sel.[b] (%)
1	**7a**	BINOL	1	98.6	>99.9
2	**7a**	**6**	1	>99	99.4
3	**7a**	**6**	1	41.8	>99.9[c]
4	**7a**	**6**	1	67.8	99.6[d]
5	**7a**	**6**	1	44.2	88.7[e]
6	**7a**	**6**	1	78.7	99.9[f]
7	**8a**	**6**	1	96.7	98.6
8	**9a**	**6**	1	85.1	92.5
9	**10a**	**6**	1	85.7	99.7
10	**11a**	**6**	1	>99	95.4
11	**7a**	SBA-15	1	>99	90.6
12	**7a**	BINOL + TM-SBA-15	1	>99	95.0
13	**7a**	**6**	2	98.4	>99.9[g]
14	**7a**	**6**	3	98.0	>99.9[g]
15	**7a**	**6**	4	98.7	98.4[g]
16	**7a**	**6**	5	97.9	94.7[g]

[a] Reactions were carried out using a MAS-1 single mode cavity microwave (continuous irradiation: 2.45 GHz, power: 700 W). *Reaction conditions*: ligands (0.015 mmol), titanium(IV) isopropoxide (0.015 mmol), tetraallyltin (0.041 mmol), aldehydes (0.15 mmol), reaction time (15 min). [b] Conversion of products on the basis of starting material (aldehydes) and selectivity determined by HPLC peak area integration at 210 nm. [c] Data were obtained without titanium(IV) isopropoxide. [d] Data were obtained using isopropanol as solvent; reaction time (12 h). [e] Data were obtained using water as solvent; reaction time (12 h). [f] Data were obtained using 5% mol of catalyst. [g] Recovered ligands were used.

Because pure SBA-15 contains large amounts of Si–OH groups, it is not only a simple medium but also a mild acid catalyst or an accelerator. In order to demonstrate the effect of Si–OH groups and to compare catalytic performance, two control experiments were carried out using pure SBA-15 and BINOL plus TM-SBA-15 (SBA-15 with trimethylsilylated end-capping of Si–OH groups) as ligands under similar reaction conditions. It was found that the former afforded the corresponding alcohol in 90.6% selectivity, while the latter gave the corresponding alcohol in 95.0% selectivity (entries 11 and 12). Apparently, the latter was a better alkylating reagent than the former, suggesting that BINOL was more efficient in such catalysis. In comparing both cases with the mesoporous silica-supported BINOL ligand **6**, the high chemoselectivity of **6** indicated the advantage of regularly organizing BINOL ligands on a highly ordered mesoporous material (entry 2 *vs.* entries 11 and 12). This was mainly due to the regularly dispersed arrangement of the catalytic species. This kind of arrangement did not only offer reasonable space for recognition of the substrates, but also restricted aggregation of the catalytic species, resulting in a high efficiency in catalytic allylation reaction.

An important feature of the design of ligand **6** is the easy and reliable separation *via* simple filtration. For example, upon completion of the reaction, the catalyst was quantitatively recovered *via* filtration. The recycled catalyst still afforded high catalytic activity and selectivity (entries 13–16).

Therefore, employing the mesoporous silica-supported BINOL ligand **6** to promote the catalytic allylation under microwave irradiation in solid media, the following conclusions can be drawn. First, the microwave radiation can accelerate obviously the catalytic allylation reaction, which is not only convenient but also environmentally friendly. Second, the regularly immobilized ligands on the highly ordered mesoporous materials can enhance effectively chemoselectivity due to the regularly dispersed arrangement of the catalytic species. Third, the highly ordered mesoporous catalyst can be recovered and reused without serious loss of its activity and selectivity, in which neither extraction nor chromatographic separation is necessary.

In conclusion, we describe an efficient and operationally simple method for the catalytic allylation of aromatic aldehydes under microwave irradiation in solid media. The catalyst derived from a mesoporous silica-supported ligand **6** showed excellent catalytic activities and high selectivities for the allylation of aromatic aldehydes. Furthermore, such catalysts could be recovered and reused five times without serious loss of its activity and selectivity, showing good potential in industrial application.

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