

Microwave-assisted tandem allylation-isomerization reaction catalyzed by a mesostructured bifunctional catalyst in aqueous media

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A mesoporous silica-supported bifunctional Ti-Ru-SBA-15 catalyst with an ordered two-dimensional hexagonal mesostructure was prepared by postmodifying organometallic complexes $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{Ti}(\text{O}^i\text{Pr})_4$ onto PPh_2 -SBA-15. During the tandem addition-isomerization reaction of benzaldehyde under microwave irradiation in aqueous media, the mesoporous silica-supported Ti-Ru-SBA-15 catalyst exhibited high catalytic activity (more than 97%) and selectivity (up to 96%). Such a catalyst could be recovered easily and used repetitively five times without significantly affecting its catalytic activity and selectivity.

Introduction

The tandem reaction has a significant impact on the manufacture of fine chemicals and pharmaceutical intermediates due to atom economy and minimum workup. A number of tandem reactions employing homogeneous bimetal complexes as catalysts have been reported in the literature.¹ However, apart from complicated catalyst compatibility with residual materials (solvent, additives and other catalysts) in solution, these homogeneous bimetal catalysts are often difficult to recycle. To overcome these problems, a practical strategy is to immobilize them onto supports.² An immobilization strategy does not only eliminate complicated interactions, but also solves recovery and reuse of catalyst. More importantly, this kind of strategy can provide more clean product due to less product contamination caused by metal leaching. Mesoporous materials as a kind of ideal support for immobilization of catalysts have showed some salient features.³ These mesoporous silica-supported catalysts possess a high surface area and ordered mesopore channels, which are beneficial to enhancement of loading amounts and dispersion of catalytically active sites. Furthermore, they also have remarkable thermal and mechanical stability, and are easy and reliable to reuse *via* simple nanofiltration. Obviously, the design of mesoporous silica-supported bifunctional catalysts represents a rapidly growing field that is on the verge of being applied in industry.

Catalytic allylation of carbonyl compounds⁴ and isomerization of homoallylic alcohols⁵ are two important methods to prepare alcohols, which serve as important fundamental building blocks in many biologically active compounds. Exploration of their industrial applications has led to great development in nontraditional technologies and methodologies for cleaner and more benign chemical processes based on environmental demands. Microwave-assisted catalytic technology⁶ and aqueous methodology⁷ for organic reactions have been well-known

to be environmentally friendly in these fields. A number of successful examples have appeared in the literature.^{8–10} Among these catalysts, titanium complexes are highly efficient allylation catalysts⁹ while ruthenium complexes are extensively employed in catalytic isomerization of allylic alcohols.¹⁰ Although fruitful achievements have been obtained in each research field, however, the tandem Ti/Ru-catalyzed allylation-isomerization reaction employing immobilization strategy in aqueous medium, especially introduction of microwave-assisted catalytic technology, is not available.

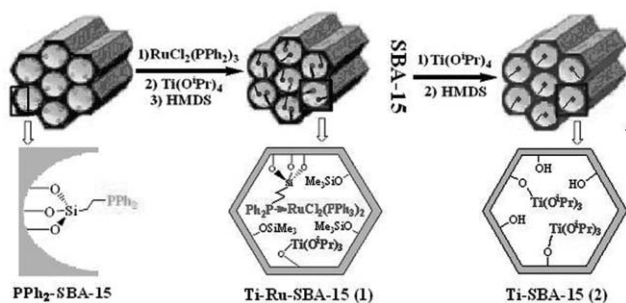
Recently, we have reported a series of mesoporous catalysts and their applications in green catalytic processes.¹¹ Especially, microwave-assisted Ti-catalyzed allylation of aldehydes has showed highly catalytic activity in solid media.^{9e} As an extension of our previous studies, we herein develop a facile preparation of mesoporous silica-supported bifunctional catalyst **1** by a postmodification method based on PPh_2 -SBA-15,^{11b} and apply it to the microwave-assisted tandem Ti/Ru-catalyzed allylation-isomerization reaction of benzaldehyde in aqueous media. The research focuses on the following: (1) construction of a highly ordered mesoporous silica-supported bifunctional Ti-Ru-SBA-15 catalyst; (2) investigation of its catalytic performance in the tandem allylation-isomerization reaction in aqueous media.

Experimental

General

The mesoporous silica-supported catalyst, abbreviated as Ti-Ru-SBA-15 (**1**), was prepared by a postmodification method. As shown in Scheme 1, Ru-SBA-15 was prepared by the reaction of PPh_2 -SBA-15 with $\text{RuCl}_2(\text{PPh}_3)_3$ following the reported method.^{11b} $\text{Ti}(\text{O}^i\text{Pr})_4$ was then anchored onto Ru-SBA-15 followed by protection of the silicon-hydroxyl groups using HMDS as reagents¹² to afford the mesoporous silica-supported bifunctional catalyst Ti-Ru-SBA-15 (**1**) as a light yellow powder. For comparison, Ti-SBA-15 (**2**) was also synthesized according to a similar method.

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Scheme 1 Synthesis of 1 and 2.

Catalyst preparation

Preparation of Ti-Ru-SBA-15 (1). Ru-SBA-15 [(pore size of 5.5), 1.0 g] was dehydrated at 125 °C under 0.01 Torr for 4 h before addition of the fresh titanium(IV) isopropoxide (0.50 mL, 1.45 mmol) in dry toluene (20 mL). The resulting mixture was stirred and refluxed for 24 h under an argon atmosphere, during which time titanium(IV) isopropoxide was grafted onto the supports. After being cooled, filtrated, and washed thoroughly with toluene and CH_2Cl_2 , the solids were transferred to a fresh Schlenk. Then a solution HMDS $[(\text{CH}_3)_3\text{Si}]_2\text{N}$ (5.0 mL, 25.0 mmol) in 25 mL dry toluene was slowly added to this Schlenk. The resulting suspension was stirred overnight. Then the residues were filtrated and washed twice with dry toluene. After Soxlet extraction in toluene solvent to remove unreacted starting materials, the solid was dried under reduced pressure overnight to afford **1** (1.06 g, 14.5% relative to titanium(IV) isopropoxide) in the form of a light yellow powder. IR (KBr) cm^{-1} : 3441 (s), 3076 (w), 2958 (w), 2869 (w), 1650 (m), 1625 (w), 1433 (w), 1320 (w), 1086 (s), 952 (w), 848 (m), 804 (w), 756 (w), 694 (w), 565 (w), 461 (m) cm^{-1} ; Ru contents: 33.2 mg/g (0.33 mmol/g); Ti contents: 56.4 mg/g (1.18 mmol/g); Anal. Found: C 30.07, H 3.22; S_{BET} : 347 m^2/g , V_{pore} : 0.47 cm^3/g , d_{pore} : 3.4 nm; ^{29}Si MAS/NMR (79.5 MHz): Q^4 ($\delta = -114$ ppm), Q^3 ($\delta = -103$ ppm) and T^3 ($\delta = -72$ ppm); ^{13}C CP/MAS (100.6 MHz): 16.8, 26.3, 61.2, 69.7 and 131.4 ppm.

Preparation of Ti-SBA-15 (2). SBA-15 [(pore size of 7.6), 1.0 g] was dehydrated at 125 °C under 0.01 Torr for 4 h before the addition of the fresh titanium(IV) isopropoxide (0.50 mL, 1.45 mmol) in dry toluene (20 mL). The resulting mixture was stirred and refluxed for 24 h under an argon atmosphere, during which time titanium(IV) isopropoxide was grafted onto the supports. Then the residues were filtrated and washed twice with dry toluene. After Soxlet extraction in toluene solvent to remove unreacted start materials, the solid was dried under reduced pressure overnight to afford **2** (1.07 g, 17.0% relative to titanium(IV) isopropoxide) in the form of a white powder. IR (KBr) cm^{-1} : 3428 (s), 2986 (w), 2913 (w), 2851 (w), 1634 (m), 1512 (w), 1447 (w), 1343 (w), 1076 (s), 951 (w), 848 (m), 804 (w), 753 (w), 694 (w), 565 (w) cm^{-1} ; Ti contents: 61.5 mg/g (1.28 mmol/g); Anal. Found: C 21.04, H 1.57; S_{BET} : 431 m^2/g , V_{pore} : 0.51 cm^3/g , d_{pore} : 5.1 nm; ^{29}Si MAS/NMR (79.5 MHz): Q^4 ($\delta = -111$ ppm), Q^3 ($\delta = -103$ ppm) and Q^2

($\delta = -93$ ppm); ^{13}C CP/MAS (100.6 MHz): 16.6, 25.1, 58.9 and 68.1 ppm.

Characterization

Ru and Ti content was analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). X-ray powder diffraction (XRD) experiments were carried out on a Rigaku D/Max-RB diffractometer with $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM2010 electron microscope, operated at an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. Nitrogen adsorption isotherms were measured at 77 K after being outgassed at 423 K overnight on a Quantachrome Nova 4000 analyzer. Pore size distributions and specific surface areas (S_{BET}) were calculated using BJH model and BET method, respectively. Solid-state ^{29}Si MAS NMR and ^{13}C CP MAS NMR spectra were recorded on a Bruker AV-400 spectrometer.

Activity test

Catalytic isomerization of 1-phenyl-3-buten-1-ol under microwave irradiation in aqueous media. 1-phenyl-3-buten-1-ol (0.025 mL, 0.25 mmol) was added to a suspension of Ti-Ru-SBA-15 (**1**) (42.6 mg, 0.014 mmol, based on Ru from ICP; 0.050 mmol, based on Ti from ICP) in 2 mL of water at room temperature in a thick walled Pyrex tube. When the addition was complete, the tube was positioned in a MAS-2 single mode cavity microwave with a water-cooled condenser from Sineo Microwave Chemistry Technology (China) Co. LTD, adjusting the reaction temperature button at 100 °C and producing continuous irradiation at 2.45 GHz, and the mixture was irradiated with 700 W for 10 minutes. Then 2 mL of ethyl acetate was added. After being filtrated, the organic layer was dried over Na_2SO_4 and concentrated. The residue was further purified by flash column chromatography on silica gel (eluent: ethyl acetate/hexane = 1:4) to afford 4-phenyl-3-buten-2-ol as a colorless liquid.

Catalytic tandem allylation-isomerization reaction under microwave irradiation in aqueous media. Tetraallyltin (0.015 mL, 0.065 mmol) and benzaldehyde (0.025 mL, 0.25 mmol) was added to a suspension of Ti-Ru-SBA-15 (**1**) (42.6 mg, 0.014 mmol, based on Ru from ICP; 0.050 mmol, based on Ti from ICP) in 2 mL of water at room temperature in a thick walled Pyrex tube. When the addition was complete, the tube was positioned in a MAS-2 single mode cavity microwave with a water-cooled condenser from Sineo Microwave Chemistry Technology (China) Co., LTD, adjusting the reaction temperature button at 100 °C and producing continuous irradiation at 2.45 GHz, and the mixture was irradiated with 700 W for 10 minutes. Then 2 mL of ethyl acetate was added. After being filtrated, the solid was washed several times with ethyl acetate, and finally dried at 85 °C under vacuum for recycling-experiments. The the organic layer was dried over Na_2SO_4 and concentrated. The residue was further purified by flash column chromatography on silica gel (eluent: ethyl acetate/hexane = 1:4) to afford 4-phenyl-3-buten-2-ol as a colorless liquid.

Results and discussion

FTIR spectra of **1–2** are shown in Fig. 1. Besides the general characteristic peaks of pure SBA-15, the catalyst **1** displays similar peaks when compared to Ru-SBA-15 observed in the literature.^{11b} The main differences are that the catalyst **1** displays an abrupt decrease of band intensity around 3441 cm⁻¹, suggesting substitution of a large fraction of surface OH groups by methyl groups. The ²⁹Si CP/MAS NMR measurements (Fig. 2) show clearly that **1** presents two strong Q peaks [Q⁴ (−114 ppm), Q³ (−103 ppm)] and a medium T³ peak (−72 ppm) while **2** only gives Q peaks [Q⁴ (−111 ppm), Q³ (−103 ppm) and Q² (−93 ppm)]. As compared with typical isomer shift values of −48.5, −58.5 and −67.5 ppm for T³/T²/T¹ signals (T³{RSi(OSi)₃}, T²{R(HO)Si(OSi)₂} and T¹{R(HO)₂Si(OSi)}), and of −91.5, −101.5, −110 ppm for Q⁴/Q³/Q² signals (Q⁴{Si(OSi)₄}, Q³{(HO)Si(OSi)₃} and Q²{(HO)₂Si(OSi)₂}),¹³ the strong Q⁴, Q³ peaks and the relatively weak T³ peak in **1** suggest that **1** possesses mainly a network structure of

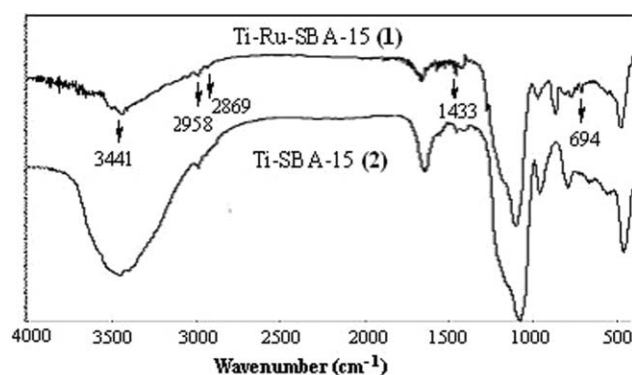


Fig. 1 IR spectra of **1** and **2**.

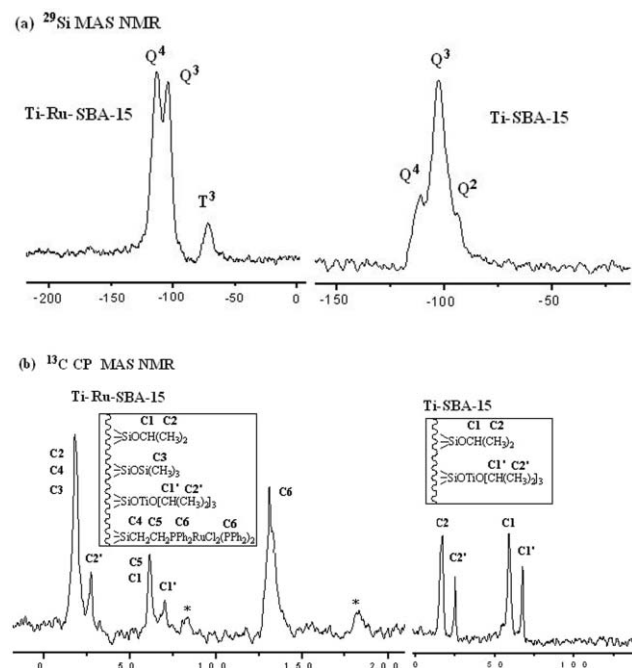


Fig. 2 The solid-state NMR spectra of **1** and **2**. (a) ²⁹Si MAS NMR and (b) ¹³C CP MAS NMR.

{Si(OSi)₄} and {(HO)Si(OSi)₃} and the formation of RSi(OSi)₃ (R = organometallic complexes) as a part of the wall in the mesoporous structure. The ¹³C CP/MAS NMR spectrum of **1** displays a peak at 131.4 ppm for benzene rings, and at 16.8, 26.3, 61.2 and 69.7 ppm for the others, which are marked in Fig. 2b. The ¹³C CP/MAS NMR spectrum of **2** further confirms these chemical shift values (16.6, 25.1, 58.9 and 68.1). For comparison, it is easily found that there are two groups of aliphatic carbon atoms of isopropoxide, corresponding to Ti-OⁱPr and Si-OⁱPr groups, as marked in Fig. 2b. From the intensity of peaks in **1**, the peaks at 16.8 ppm and 61.2 ppm corresponding to Ti-OⁱPr groups are obviously enhanced. The enhanced peaks indicate that carbon atoms of the -PCH₂CH₂Si- moiety and -SiMe₃ groups are overlapped, in which the shift values around 16.8 ppm are ascribed to the carbon atoms of the -CH₂Si- and -SiMe₃ groups, and around 61.2 ppm are attributed to the carbon atom of the -PCH₂- groups. All these observations confirm the successful postmodification of organometallic complexes onto the mesoporous support.

Fig. 3 shows XRD patterns of **1** and **2**. Similar to PPh₂-SBA-15 and Ru-SBA-15,^{11b} **1** and **2** also exhibit one intense *d*₁₀₀ diffraction and two weak peaks indicative of *d*₁₁₀ and *d*₂₀₀ diffractions, implying that the ordered hexagonal mesostructure (*p6mm*) could be well preserved.¹⁴ The TEM morphologies further confirm that **1** and **2** have well-ordered mesostructures with the hexagonal arrangement as shown in Fig. 4. Nitrogen adsorption-desorption isotherms of **1** and **2** in Fig. 5 exhibit typical IV type N₂ adsorption-desorption isotherms with a H₁ hysteresis loop and a visible step at *P*/*P*₀ = 0.40–0.80, corresponding to capillary condensation of nitrogen in mesopores. The incorporation of Ti(OⁱPr)₄ onto SBA-15 or Ru-SBA-15 causes a slight decrease in mesopore size, surface area, and pore volume when compared to data in the literature, obviously due to coverage of pore surface with the organometallic complexes, leading to an increase of the wall thickness.^{11b}

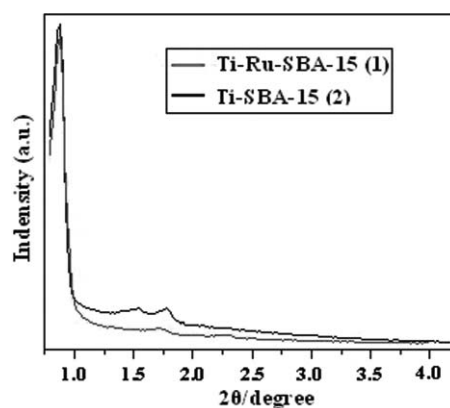


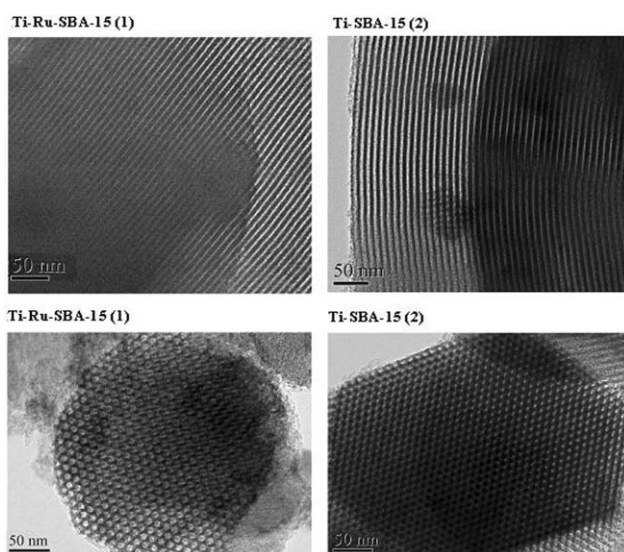
Fig. 3 The powder XRD patterns of **1** and **2**.

With the mesoporous silica-supported catalyst **1** in hand, we firstly examined its catalytic isomerization of 1-phenyl-3-buten-1-ol under microwave irradiation in aqueous media. These results are collected in Table 1. Because such a reaction has a marked dependence on the molar ratio of the Ru(II)/substrate,¹⁵ a few reaction conditions are screened. From entries 3–5, one can see

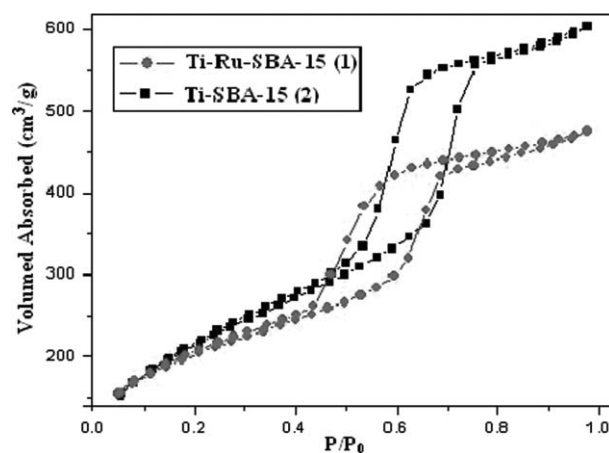
Table 1 Microwave-assisted catalytic isomerization of 1-phenyl-3-buten-1-ol^a

Entry	Catalyst	Ru content (%)	Time (min)	Conv. (%) ^b	Select. (%)
1	RuCl(PPh ₃) ₃	5.6	1200(10)	79(99.9)	95 ^c (97.7)
2	Ru-SBA-15	5.6	1200(10)	77(99.8)	94 ^c (97.5)
3	1	2.4	10	92.7	88.9
4	1	4.0	10(180)	93.4(87)	92.3(95) ^d
5	1	5.6	10(10)	96.3(99.4)	97.4(73.8) ^e
6	1	7.2	10	99.4	73.8

^a Reaction conditions: MAS-2 single mode cavity microwave with a water-cooled condenser, catalyst (42.6 mg, 0.014 mmol, based on Ru from ICP), 1-phenyl-3-buten-1-ol (0.25 mmol), reaction time (10 min), and reaction temperature 100 °C. ^b HPLC yields. ^c Data were obtained from the literature without microwave irradiation.^{11b} ^d Data were obtained from the literature without microwave irradiation.¹⁵ ^e Data were obtained from the literature under microwave irradiation in solid media.

**Fig. 4** The TEM images of **1** and **2** viewed along the [100] and [001] directions.

easily that the isomerization reactions employing 2.4%, 4.0% and 5.6% Ru(II) metal (based on the data from ICP) afford 88.9%, 92.3% and 97.4% selectivity, respectively. Apparently, increasing the amounts of catalyst result in increasing selectivity in product formation. However, further increased amounts of catalyst to 7.2% lead a low selectivity (entry 6). Although the selectivity of catalyst **1** is slightly low when compared to the parent catalyst employing 4.0% Ru(II) metal reported in the literature (entry 4 *versus* entry 4 shown in bracket),¹⁵ the selectivity employing 5.6% Ru(II) metal is better than that obtained using the corresponding Ru-SBA-15 catalyst without microwave irradiation (entry 5 *versus* entries 1–2),^{11b} and is nearly the same as that obtained using the corresponding Ru-SBA-15 catalyst and the parent homogeneous catalyst with microwave irradiation (entry 5 *versus* entries 1 and 2 shown in brackets). More importantly, the catalytic isomerization reaction under microwave irradiation can

**Fig. 5** Nitrogen adsorption-desorption isotherms of **1** and **2**.

be completed at a much shorter reaction time (10 minutes). Such a reaction rate is much faster than the corresponding Ru-SBA-15 and the parent catalyst without microwave irradiation, suggesting the microwave radiation can obviously accelerate the catalytic isomerization reaction. In order to test the role of water in the catalytic process, the isomerization of 1-phenyl-3-buten-1-ol under microwave irradiation in solid media is also carried out. It is found that 99.4% conversion and 73.8% selectivity are obtained (entry 5 shown in brackets). Although the conversion increases slightly, the selectivity is low when compared to that in aqueous media (entry 5 *versus* entry 5 in brackets), which is due to the increase of the by-product **3c**. Such a result suggests that the oxidation derived from the locally high temperature under microwave irradiation in solid media might be responsible for this phenomenon.

On the basis of the optimized molar ratio of Ru(II)/substrate, we then tested the tandem reaction, catalytic allylation of benzaldehyde followed by isomerization, under microwave irradiation in aqueous media. In order to afford almost pure allylated product and to prevent pollution from large amounts of hydrolyzed inorganic tin compounds during work-up stage, a small excess of tetraallyltin as nucleophile reagent is employed.^{11c,16} As can be seen from Table 2, benzaldehyde is cleanly reacted with 0.28 equiv. of tetraallyltin to provide the product **3b** in 98.8% conversion and 95.5% selectivity (entry 1) with a small amount of by-product **3a** and **3c**, which was obviously better than those obtained using Ti-Ru-SBA-15 in organic solvent and in water without microwave irradiation under the similar reaction conditions (entries 2 and 3). Such a tandem allylation-isomerization reaction could also be completed with the same result on a large scale using 10.0 mmol of benzaldehyde as substrate. In order to explore the nature of the catalytic performance, two control experiments were also carried out using Ti-SBA-15 and PPh₂-SBA-15 plus RuCl₂(PPh₃)₃ as catalysts under the similar reaction conditions. It is found that no product **3b** is observed in the former (main by-product **3a**), while 90.3% selectivity is obtained in the latter (entries 4 and 5). The former suggests that the isomerization reaction is triggered from the ruthenium complexes, while the latter indicates that the randomly oriented RuCl₂(PPh₃)₃ onto materials results in catalytic performance that is further proved using Ru-SBA-15 as a catalyst with 92.1% selectivity (entry 6). Comparing the latter with the mesoporous

Table 2 Microwave-assisted tandem allylation-isomerization reaction of benzaldehyde^a

Entry	Catalyst	Run	Conv. (%) ^b	Select. (%)
1	1	1	98.8	95.5
2	1	1	87.5	56.5 ^c
3	1	1	76.4	38.1 ^d
4	2	1	>99	9.7 ^e
5	PPh ₃ -SBA-15 + RuCl ₂ (PPh ₃) ₃	1	99.5	90.3
6	Ru-SBA-15	1	98.7	92.1
7	1	2	98.4	95.4 ^f
8	1	3	99.2	94.3 ^f
9	1	4	99.2	91.5 ^f
10	1	5	97.4	91.0 ^f

^a Reaction conditions: MAS-2 single mode cavity microwave with a water-cooled condenser, catalyst (42.6 mg, 0.014 mmol, based on Ru from ICP; 0.050 mmol, based on Ti from ICP), tetraallyltin (0.065 mmol), benzaldehyde (0.25 mmol), reaction time (10 min), and reaction temperature 100 °C. ^b HPLC yields. ^c Data were obtained using isopropanol as solvent without microwave irradiation; reaction time (20 h). ^d Data were obtained using water as solvent without microwave irradiation; reaction time (20 h). ^e Data were obtained using **2** (39.1 mg (0.10 mmol), based on Ti from ICP) under similar conditions. ^f Recovered catalyst was used.

silica-supported Ti-Ru-SBA-15 catalyst, the higher selectivity of Ti-Ru-SBA-15 and Ru-SBA-15 than the latter are due to the regularly dispersive arrangement of the catalytic species onto a highly ordered mesoporous materials. Such an arrangement does not only restrict aggregation of the catalytic species but also is beneficial to recognition of the substrate, resulting in a high efficiency of the catalytic reaction.

More importantly, the design of the mesoporous silica-supported bifunctional catalyst Ti-Ru-SBA-15 is easy and reliable to separate *via* simple filtration. For example, upon completion of the reaction, the catalyst **1** is quantitatively recovered *via* filtration. The recycling catalyst can be reused five times without obviously affecting its catalytic activity and selectivity, which is due to the slight loss of metal confirmed by ICP analysis after five recycles (entries 7–10).

Conclusions

In summary, we have developed an efficient method for the tandem allylation-isomerization reaction of benzaldehyde under microwave irradiation in aqueous media. The mesostructured bifunctional catalyst showed high catalytic activity and selectivity. Furthermore, such a catalyst could be recovered and reused five times without loss of its catalytic activity and selectivity.

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