Catalysis Communications 11 (2010) 487–492

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Liquid phase hydrogenation of olefins using heterogenized ruthenium complexes as high active and reusable catalyst

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ARTICLE INFO

Article history:
Received 13 September 2009
Received in revised form 26 November 2009
Accepted 3 December 2009
Available online 6 December 2009

Keywords:
Ru complexes
Tannin
Heterogeneous
Liquid phase hydrogenation

ABSTRACT

The homogeneous ruthenium complexes were immobilized onto tannin grafted micelle templated silica (MTS–BT) to prepare heterogeneous MTS–BT–Ru catalysts. The catalyst was found to be highly active in liquid phase hydrogenation of olefins. The heterogenized Ru complexes also exhibited excellent stability, reusability and catalytic efficiency. Furthermore, this methodology could extend to heterogenize other complexes to improve their reusability and stability.

1. Introduction

Homogeneous ruthenium (Ru) complexes have been widely used as catalysts in various catalytic reactions such as hydrogenation [1], oxidation [2] and isomerization [3]. Homogenous Ru complexes have the advantage of high catalytic activity, but difficult separation from the catalytic media limits their commercial development and practical application [4]. To overcome this disadvantage, Ru complexes are often immobilized onto water-insoluble matrices to prepare heterogeneous Ru complexes [5,6]. The obtained heterogeneous Ru catalysts are easily recovered by filtration and can be reused many times without a significant loss of activity, which is preferred from both environmental and economical perspectives. Additionally, heterogeneous catalysts sometime have shown even higher catalytic activity/selectivity in comparison to unsupported analogues due to that the interactions of catalytic active sites with the supports can result in steric hindrance and/or chemoselectivity [7,8].

Polymeric organic and inorganic supports have been widely employed for the immobilization of various homogeneous complexes. In many cases, the immobilization of homogeneous catalyst onto polymeric support renders reduced activity that decreases the overall catalytic efficiency of the catalyst, mainly due to the swelling and/or deformation of the organic polymer [9–11]. Inorganic supports are particularly suitable matrices owing to their high mechanical strength, chemical inertness and swelling resistance in different organic solvent [12]. For example, metal species can be immobilized onto silica matrix to prepare heterogenized catalysts [13,14]. However, the heterogenized catalytic species on the inorganic supports are sometimes leached out during reaction process, which drastically decreases the reusability of the catalysts [15]. As a result, much effort is currently devoted to the development of an adequate methodology to stably immobilize homogenous complexes onto inorganic supports.

Micelle templated silica (MTS) is one of the most commonly used inorganic supports, which is characterized by high thermal and mechanical stability. MTS can be easily functionalized by direct grafting of functional organosilane groups on their surfaces [16,17], but polar solvent including water and alcohols can promote the hydrolysis of the grafted moieties that negatively affect the stability of the catalyst. One promising way to address these issues is to prepare more stable and hydrolysis-resistant organic–inorganic hybrid support, where the organic polymers or ligands are grafted onto the surface of inorganic support, and the catalytic species can be subsequently anchored by the polymers or ligands [18]. Ideally, the polymers should be covalently grafted onto inorganic support, and also have proper compatibility towards the catalytic species. If the interaction between the polymers and the catalytic species is too strong, the activity of the catalyst will be drastically decreased, otherwise the catalytic species are easily leached out during the reaction process. Consequently, the selection of organic polymer is a key factor to fabricate organic–inorganic support.

Tannins, one of the most abundant biomass resources, are the soluble polyphenols with a large number of adjacent phenolic

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doi:10.1016/j.catcom.2009.12.006

hydroxyls, and can be easily obtained from the extraction of plants. According to the chemical structure of tannins, they are classified into hydrolyzable tannins and condensed tannins. The general characteristics of tannins are that they are able to chelate with many kinds of metal ions through their dense ortho-phenolic hydroxyls [19–21], and have no swelling or deformation in polar solvent. Additionally, tannins can be covalently grafted onto $-NH_2$ containing inorganic supports through the Mannich reaction. All these properties suggest that tannins are ideal polymers for the preparation of organic–inorganic hybrid support. In this study, we developed a route for the grafting of bayberry tannin (BT, a kind of typical condensed tannin) onto MTS, and then anchored Ru complexes onto MTS–BT to prepare heterogeneous Ru catalysts (MTS–BT–Ru). The objective of the present work is therefore to investigate the catalytic activity of MTS–BT–Ru for the liquid phase hydrogenation of olefins, as well as its stability and reusability.

2. Experimental

2.1. Reagents

Cyclohexane, *n*-hexanol, tetraethyl orthosilicate (TEOS), 3-aminopropyl-triethoxysilane (APES), glutaraldehyde, ruthenium chloride ($RuCl_3 \cdot nH_2O$) and other chemicals were all analytic reagents. BT was obtained from the barks of *myrica esculenta* by extraction with an acetone–water solution (1:1, v/v) and then spray dried. The tannin content of the extract was determined to be 76.3% according to Hide Powder Method, a national standard method of China (Code: GB2615–81).

2.2. Preparation of MTS

MTS was prepared following a methodology similar to that described by Cheng et al. [22]. Briefly, 1 mL of *n*-hexanol, 1 mL of Triton X-100 and 4 mL of cyclohexane were added into 500 mL deionized water with vigorous stirring to obtain emulsion solution. Then, 8 mL of TEOS (silica source) and 2 mL of APES (aminating agent) were added into the emulsion solution, followed by vigorous stirring at 303 K for 2 h. A proper amount of ammonia was drop-wise added into the solution to promote the hydrolysis of silica precursor, and then the mixture was further stirred at 303 K for another 2 h. Afterwards, 2 mL of acetone, used as the emulsion breaker, was added into the emulsion. When the breaking of the emulsion was completed, the MTS was collected by filtrating, washed thoroughly with deionized water and dried in vacuum at 353 K for 24 h.

2.3. Preparation of MTS–BT

BT (0.1 g) was dissolved in 50 mL deionized water, and then mixed with 1.0 g of MTS prepared above, followed by constant stirring at room temperature for 2 h. About 2 mL of glutaraldehyde (50%, w/w) was drop-wise added into the mixture under constant stirring in order to graft BT onto MTS. After reaction for 12 h at 313 K, MTS–BT were collected by filtration, fully washed with deionized water and dried in vacuum at 303 K for 24 h. The concentration of BT in solutions was analyzed by ultraviolet–visible spectrum (UV–Vis, TU-1901), and the grafting degree of BT on MTS–BT was defined as:

$$\frac{\text{Amount of BT(g)grafted onto MTS(g)}}{\text{Amount of MTS(g)}} \times 100\%.$$

As a result, the grafting degree of BT on the MTS–BT was approximately 8.7%.

2.4. Preparation of MTS–BT–Ru

MTS–BT (1.0 g) was added into 20 mL of $RuCl_3$ solution at pH 2.0, where the concentration of Ru(III) was 500.0 mg/L. The reaction was conducted at 303 K with constant stirring for 24 h. Then, MTS–BT–Ru was obtained after fully washed with deionized water and dried in vacuum at 303 K for 24 h. Based on the measurements of inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2100 DV), the Ru loading on MTS–BT–Ru was determined to be 0.96%

$$\left(\text{calculated as}: \frac{\text{Initial amount of Ru(III)(g)} - \text{Residual amount of Ru(III)(g)}}{\text{Amount of MTS(g)}} \times 100\%\right).$$

2.5. Characterization of catalyst

Fourier Transform Infrared Spectroscopy (FTIR) of samples was analyzed using FTIR-7600 instrument. Proton Nuclear Magnetic Resonance (H NMR) spectrum of the samples was measured by Bruker DPX400 NMR instrument using DMSO-d_6 as solvent. Wide-angle X-ray diffraction (XRD) patterns of the catalysts were recorded by an X′Pert PRO MPD diffractometer (PW3040/60) with Cu Kα radiation. Transmission electron microscopy (TEM) images of the catalysts were obtained in a FEI-Tecnai G2. The specific surface area of MTS–BT–Ru was analyzed by N_2 adsorption/desorption using Surface Area and Porosity Analyzer.

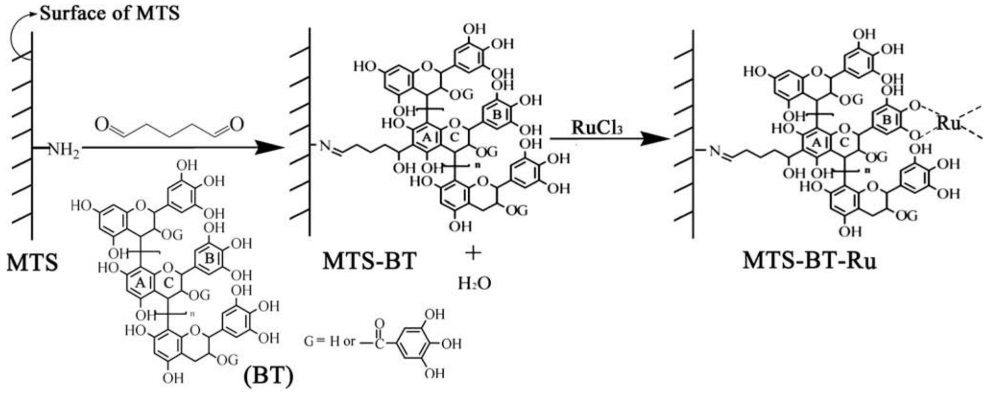
2.6. Catalytic test

The liquid phase hydrogenation of allyl alcohol was conducted in an autoclave type reactor at 1.0 MPa H_2 pressure, at a temperature of 30 °C and using 0.05 g of catalyst. In each test, 25.0 mL of methanol was used as solvent, and the obtained products were analyzed by gas chromatography (Shimadzu, GC-2010). Then, the used catalyst was recovered by filtration, thoroughly washed with methanol, and then reused. The turnover frequency (TOF) of the catalysts was calculated as: $[\text{Substrate hydrogenated(mol)}]/[\text{Ru(mol)} \times \text{t(h)}]$, and the turnover number (TON) of the catalysts was calculated as: $[\text{Substrate hydrogenated}]/[\text{Ru}]$. As control, the hydrogenation was also carried out using homogenous $RuCl_3$ complexes as the catalysts. To evaluate the universal application of MTS–BT–Ru in liquid phase hydrogenation, the hydrogenations of 2-methyl-3-buten-2ol, acrylic acid, α-methacrylic acid, styrene and cyclohexene were also carried out. As control experiments, all the olefin hydrogenations were also carried out using MTS without the immobilization of Ru

3. Results and discussion

3.1. Preparation of characterization of the catalysts

The molecular structure of BT is shown in Scheme 1. It can be seen that there are a large number of adjacent phenolic hydroxyls at the B-rings of BT, which can form chelate rings with many kinds of metal ions, and the partly attached galloyl groups at the C-rings of BT can enhance such chelating ability. Each phenolic hydroxyl at the B-rings of BT has lone electron pair, thus playing a role of strong donor to center metal ions with empty electron orbits. For this reason, the adjacent two phenolic hydroxyls of B-rings are very likely act as a bidentate ligand to bond with center metal ion forming five-membered chelate ring, which has been proved in our previous work using H NMR technique [23,24]. Since transition-metal ions have empty orbits in their electron configurations, they should be very reactive towards BT. Our research group demonstrated that BT has high affinity towards many transition-metal ions including Pd(II), Pt(IV) and Au(III) [25,26]. Considering that Ru(III) is transi-



Scheme 1. Proposed mechanism for the preparation of MTS–BT–Ru.

tion-metal ion with the electron configuration of $4d^5 5s^0$, BT also should exhibit affinity towards $RuCl_3$. On the other hand, the C6 and C8 positions of A-rings of BT have excellent nucleophilic reaction activity, and therefore, BT can form covalent bonds with the $-NH_2$ groups on the surface of MTS through a Mannich reaction by using glutaraldehyde as the cross-linking agent [27,28]. The preparation process of MTS–BT–Ru is illustrated in Scheme 1. The preparation of MTS–BT–Ru is easy to handle, and the entire process was carried out in water solution without use of organic solvent.

Fig. 1a is the FTIR spectrum of MTS–BT. The peak at 3400 cm^{-1} can be attributed to the stretching vibration of O–H bond both from silica matrix (Si–O–H) and phenolic hydroxyls of tannins (C–O–H), and its broad range is due to the formation of hydrogen bonds among BT molecules/Si–O–H. The peaks at 1627 and 1451 cm^{-1} indicate the presence of aromatic rings of tannins, which confirmed the successful grafting of BT on MTS [29]. In the FTIR spectrum of MTS–BT–Ru (Fig. 1b), the stretching vibration peak of O–H (3400 cm^{-1}) becomes relatively narrow. Considering that tannins have much stronger chelating ability towards metal ions in comparison to silica matrix (Si–O–H), the changing of peak at 3400 cm^{-1} should attribute to the interactions of phenolic hydroxyls of BT with Ru(III), which partially destroy the hydrogen bond among BT molecules, resulting in a narrow peak.

To further confirm the chelating interaction between Ru(III) and BT, Proton Nuclear Magnetic Resonance (H NMR) technique was employed. Considering the complexity of molecular structure of BT, pyrogallic acid was used as a model compound to simulate the interaction between BT and Ru(III). Fig. 2a is the H NMR spectrum of pyrogallic acid. According to literatures [30], the peaks in the range of 8.75ppm–8.00 ppm with integral of 3 protons are assigned to the phenolic hydroxyl protons, namely H^a and H^b. Other two peaks with integral of 3 protons, ranged from 6.43 to 6.23 ppm, are attributed to the phenyl protons of H^c and H^d, respectively. The single peak at 2.50 ppm is assigned to DMSO-d_6, and that at 3.46 ppm belongs to the proton of water dissolved in DMSO-d_6. Moreover, the integral assignment of protons (H^a, H^b, H^d and H^c) is very close to 2:1:2:1, which well fits the arrangement of protons in pyrogallic acid molecule. After chelated with Ru(III) (Fig. 2b), the peak related to H^b disappeared and the proton integral of H^a reduced from 2.08 ppm to 1.08 ppm, while the proton integral of H^c (from 1.06 ppm to1.00 ppm) and H^d (from 2.08 ppm to 19.4 ppm) almost unchanged. These results suggest that pyrogallic acid indeed chelates with Ru(III) through its adjacent phenolic hydroxyls.

In Fig. 3, the XRD pattern of MTS–BT–Ru shows a amorphous peak of silica at 24.4°, indicating the well preservation of SiO_2 structure after the immobilization of BT. In addition, no peaks related to Ru(0) or Ru oxides are observed, which suggest that Ru(III) are stably chelated with tannins. Further TEM image of MTS–BT–Ru (Fig. 3 insets) also confirms that no Ru particles are formed on the catalyst. Based on N_2 adsorption/desorption experiment, the specific surface area of MTS–BT–Ru was determined to be 56.03 m^2/g, and its average pore size is about 22.91 nm (Fig. 4). The mesoporous structure of MTS–BT–Ru may impart the catalytic substrates an easy access to the active sites of the catalysts.

3.2. Catalytic hydrogenation

The catalytic activity and selectivity of both homogeneous $RuCl_3$ and heterogeneous MTS–BT–Ru catalysts were compared in the liquid phase hydrogenation of allyl alcohol. In general, *n*-propanol is the target-product in allyl alcohol hydrogenation, while the substrates are easily isomerized to yield acetone and/or propanal when transition-metal catalysts are used. Consequently, it is highly desirable to develop new transition-metal catalytic systems, which minimize the unwanted substrate isomerization and thus improve the hydrogenation selectivity. The experimental results are summarized in Table 1. Compared with unsupported homogeneous Ru(III) complexes, heterogeneous MTS–BT–Ru rendered slightly decreased activity, but still retained the TOF of 1210 mol mol^{-1} h^{-1}. The decreased activity may be attributed to the increased mass transfer diffusion resistance caused by the presence of BT on the surface of MTS. On the other hand, the catalytic selectivity of the heterogenized Ru(III) com-

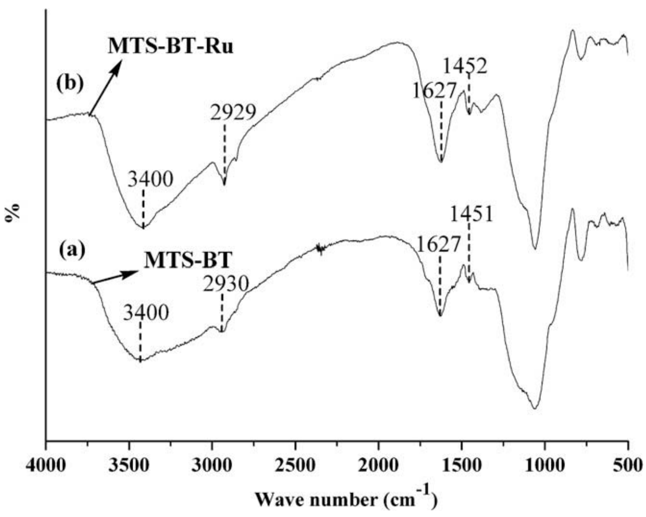


Fig. 1. FTIR spectrum of MTS–BT (a) and MTS–BT–Ru (b).

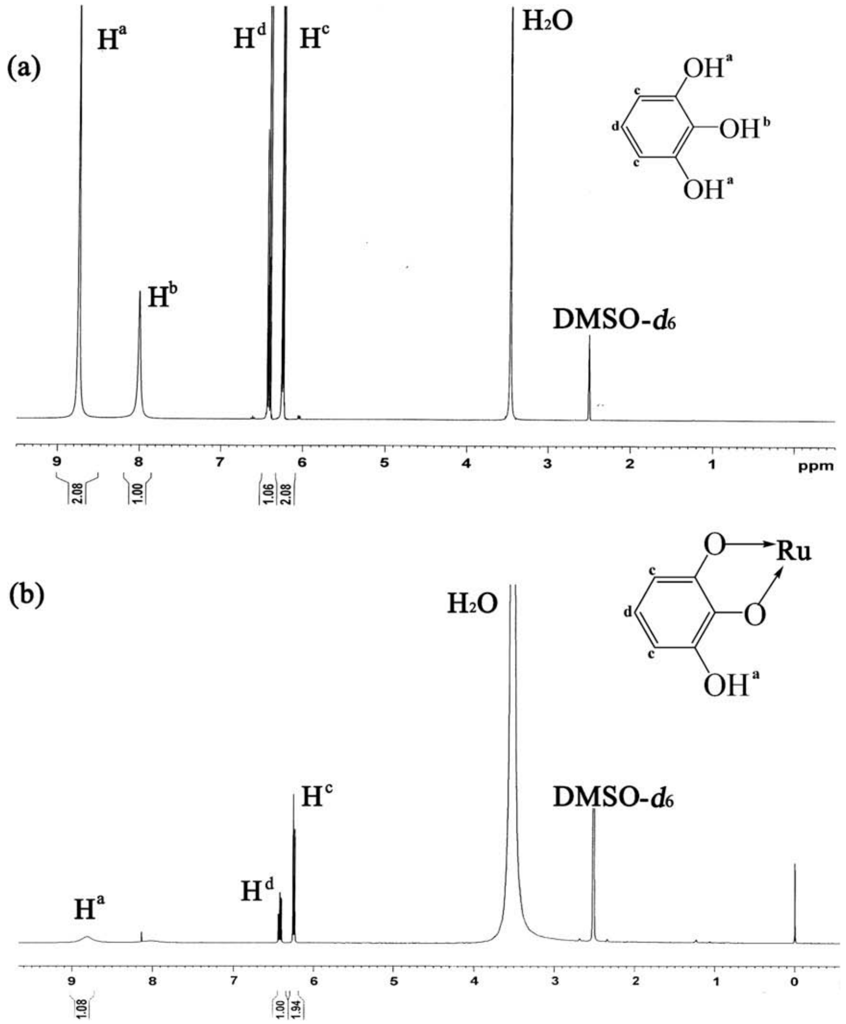


Fig. 2. H NMR spectrum of pyrogallic acid (a) and pyrogallic acid–Ru(III) (b) (DMSO-d_6, 97 K, 400 MHz).

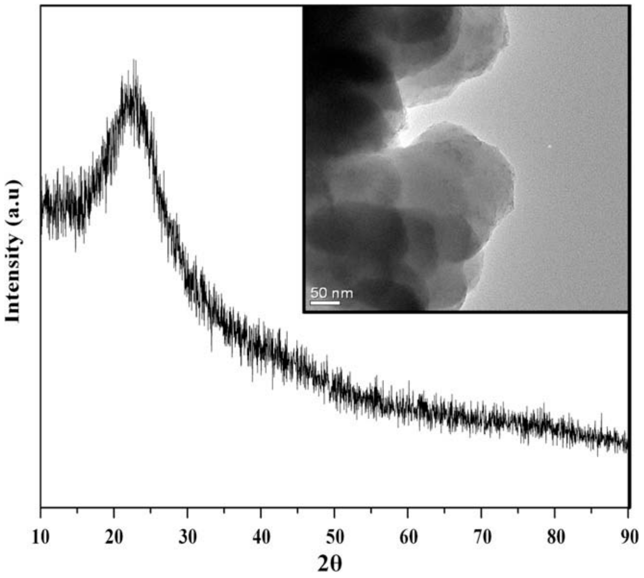


Fig. 3. XRD pattern of MTS–BT–Ru catalyst and its TEM image (insets).

plexes significantly improved. The selectivity to *n*-propanol increased from 85.6% to 92.5%, and kept a high selectivity of 91.1% at the 7th run. We believe that the presence of Ru complexes chelated with BT could affect the formation of the transition state between the ruthenium compound, the substrate and hydrogen, which may suppress the formation of by-product, resulting high selectivity. The heterogeneous MTS–BT–Ru could be reused at least

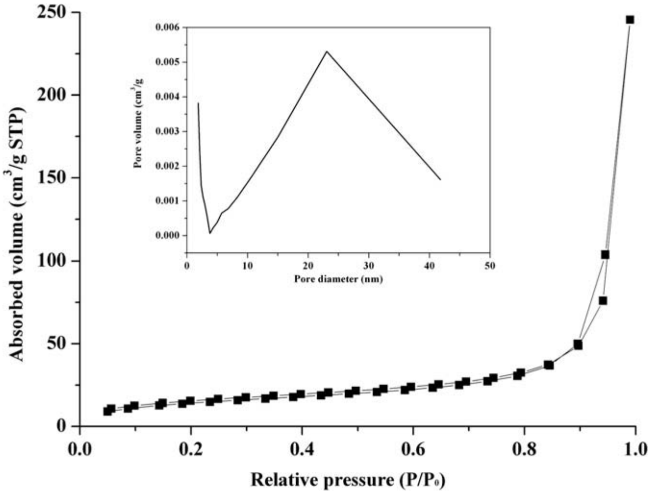


Fig. 4. N_2 adsorption/desorption isotherms and pore-size distribution plot (insets) of MTS–BT–Ru.

Table 1
Activity and selectivity between homogeneous Ru(III) and heterogeneous MTS–BT–Ru in the hydrogenation of allyl alcohol.[a]

Parameters	Homogeneous Ru(III) complexes	Heterogeneous MTS–BT–Ru	
		1-Run	7-Run
Substrate (mmol)	5	5	5
Catalyst (Ru umol)	5	5	5
Reaction time[b] (min)	85	120	130
Average TOF (mol mol^{-1} h^{-1})	1540	1210	1100
Selectivity[c] (mol%)	85.6	92.5	91.1
Substrate conversion yield (mol%)	>95	>95	>95
TON [substrate]/[Ru]	966	992	6695

[a] Reaction conditions: 30 °C, 1 MPa H_2, 25.0 mL methanol.
[b] Reaction time required for conversion >95% measured by GC.
[c] Selectivity to *n*-propanol, by-product: acetone and propanol.

7 times without significant decrease in activity. When reused 7 times, the initial activity of the catalysts is still 90.9% of the 1-run, and the final conversion yield of the substrate still reaches 95%. The leaching of Si and Ru during the hydrogenation of allyl alcohol was also analyzed using ICP-AES. It was found that no Si was detected in the solvent. In addition, the Ru leached in the solvent was no more than 3 μg for the 1st run (Supporting information 1), and no leaching of Ru was detected in the 7th run. Further FTIR analysis (Supporting information 2) revealed that no obvious change was found between the fresh catalyst and the used catalyst. All these facts confirm the stability of MTS–BT–Ru under the reaction conditions. In addition, the accumulated TON of heterogeneous MTS–BT–Ru reaches 6695, which is 6.93-fold higher than that of unsupported analogues, demonstrating its high stability and efficiency.

To evaluate the universal application of MTS–BT–Ru in liquid phase hydrogenation of olefins, a range of olefins were employed. Table 2 lists the the reaction conditions and experimental results. In can be seen that heterogeneous MTS–BT–Ru is active for olefin hydrogenation, and the conversion yields of all the substrates were higher than 95%. The olefin hydrogenation was also carried out using MTS without the immobilization of Ru, and found that MTS has no activity for all the catalytic reactions. Compared with other heterogeneous Ru catalysts [31,32], the catalytic activity of MTS–BT–Ru for liquid phase hydrogenation of olefins is appreciable. Take the hydrogenation of styrene for example, the TOF of MTS–BT–Ru under our experimental conditions (1.0 MPa H_2 and 30 °C) is as high as 2200 mol mol^{-1} h^{-1}, and the substrate conversion yield can reach 99% within 90 min. However, zeolite supported Ru complex prepared by Joseph et al. exhibited much lower TOF of 122.8 mol $mol^{-1}\cdot h^{-1}$ even the catalytic hydrogenation was performed under much higher H_2 pressure (2.8 MPa) and temperature (60 °C), and the substrate conversion yield was only 66% when the reaction was conducted 12 h [33]. On the other hand, MTS–BT–Ru exhibit size-based selectivity in some extent. Seen from Entries 1 and 2, the TOF of 2-methyl-3-buten-2ol is 570 mol $mol^{-1}\cdot h^{-1}$, which is only 41.6% of initial activity for allyl alcohol hydrogenation. Similar phenomenons are also observed in Entries 3 and 4. When α-methacrylic acid was hydrogenated, the corresponding initial TOF was only 23.38% of acrylic acid. These results suggest that BT grafted on the surface of SiO_2 may act as a filter to hinder substrate with substituent to access the active sites. During the reaction process, no solubility of the support was observed.

4. Conclusions

BT grafted MTS featuring high mechanical stability and hydrolysis-resistant has been proved to be excellent organic–inorganic hybrid support for the covalent immobilization of Ru complexes. The preparation of MTS–BT–Ru was simply achieved in aqueous solution and no additional organic solvent is needed. Compared with unsupported Ru complexes, the activity of MTS–BT–Ru is somewhat reduced but significantly improved its reusability and stability in liquid phase hydrogenation of unsaturated compounds. Considering that BT is able to chelate with various transition-metal ions, MTS–BT support can be expected to heterogenize other catalytic complexes to improve their stability and reusability.

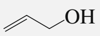
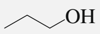
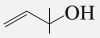
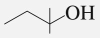
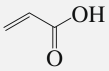
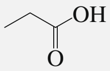
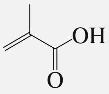
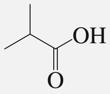
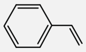
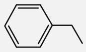
Acknowledgements

We acknowledge the financial supports provided by the Key Program of National Science Foundation of China (20536030), National Natural Science Foundation of China (20776090) and A Foundation for the Author of National Excellent Doctor Dissertation of PR. China (FANEDD200762). We also give thanks to the Test Central for the XRD, HNMR and TEM analyses.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.catcom.2009.12.006.

Table 2
Substrates and the corresponding products with catalyst MTS–BT–Ru.

Entry	Substrate	Reaction time (min)	Molar ratio substrate/Ru	Product	Selectivity (%)	Substrate conversion yield (%)	Initial TOF[c] (mol mol^{-1} h^{-1})
1[a]		120	1000:1		92.5	97	1370
2[a]		240	1000:1		100	97	570
3[a]		70	2000:1		100	97	2780
4[a]		270	2000:1		100	95	650
5[a]		90	2000:1		100	99	2200
6[b]		120	400:1		100	95	1400

[a] Reaction conditions: 30 °C, 1.0 MPa H_2, 25 mL methanol.
[b] Reaction conditions: 50 °C, 2.5 MPa H_2, 25 mL methanol.
[c] TOF was calculated when the reaction was conducted 20 min.

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