DOI: 10.1002/adsc.200505066

A Highly Active and Reusable Heterogeneous Ruthenium Catalyst for Olefin Metathesis

Liang Li, Jian-lin Shi*

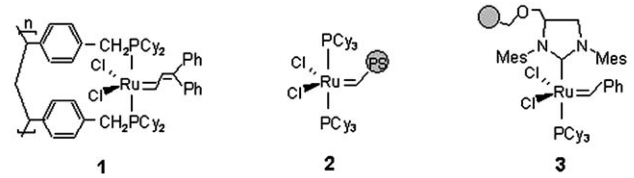
State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 DingXi Road, Shanghai 200050, People's Republic of China
Fax: (+86)-21-5241-3122; e-mail: jlshi@sunm.shcnc.ac.cn

Received: January 30, 2005; Revised: May 16, 2005; Accepted: June 22, 2005

Abstract: The synthesis and characterization of Ru complexes of the type [$L_2X_2Ru{=}CHR$] (L = PPh_3, PCy_3, N-heterocyclic carbenes or their derivates; X = Cl) grafted on mesoporous SBA-15 material are described. In this heterogeneous catalyst the Ru complexes are anchored in the pore channels of mesoporous silica material SBA-15 to prevent the decomposition of the catalytic species. Compared with formal organic-supported heterogeneous catalysts, this heterogeneous catalyst shows relatively high catalytic activity in olefin metathesis reactions and can be used several times without any decrease in catalytic activities.

Keywords: heterogeneous catalysis; immobilization; mesoporous material; N-heterocyclic carbenes; ring-closing metathesis; ruthenium

Ruthenium complexes of the type [$L_2X_2Ru{=}CHR$] (L = PPh_3, PCy_3, N-heterocyclic carbenes or their derivates; X = Cl) are highly efficient catalysts for olefin metathesis. On account of their unique properties they are increasingly used in organic synthesis as a homogeneous catalyst since being discovered by Grubbs and co-workers.[1] This precious catalyst exhibits high activity and selectivity under relatively mild conditions giving few by-products, but it is difficult to separate from the mixtures after reaction. The residual ruthenium complex may cause problems such as olefin isomerization, decomposition of the product, and increased toxicity of the final material. Therefore, it is necessary to immobilize it on solid materials to combine the advantages of conventional heterogeneous catalysts with the versatility of homogeneous ones. Up to now, different approaches have been developed in the heterogenization of this kind of catalysts in organic materials.[2] Earlier attempts by Grubbs and Nguyen to prepare polystyrene-supported catalyst **1** (see Scheme 1) achieved only limited success; it was found to be less reactive than the homogeneous one.[3] Barrett and co-workers immobilized the catalyst on vinyl polystyrene, **2**, but recycling and reuse of it cause a dramatic decrease in activity.[4] Very recently, Schürer and co-workers introduced the saturated N-heterocyclic carbene ligands to attach ruthenium catalysts onto polymer **3**, unfortunately, its reaction activity was also severely deteriorated upon reuse.[5]

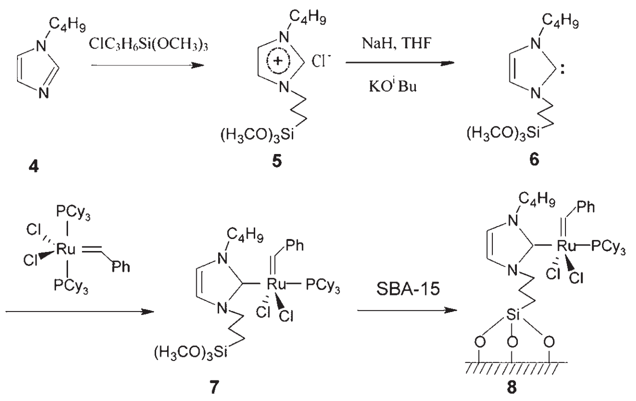


Scheme 1. Immobilized ruthenium catalysts **1**, **2** and **3**.

Through a study of the mechanism, Grubbs and Ulman have established that there was a slow but competing decomposition of the ruthenium catalytic species *via* a bimolecular pathway during the catalytic reaction.[6] Based on this proposal we prepared complex **7** (shown in Scheme 2) and anchored it in the pore channels of inorganic mesoporous silica material SBA-15 to prevent decomposition of the catalytic species.

Compared to polymers, inorganic silica material is a common support for the heterogenization of molecular catalysts due to its excellent thermal and chemical stability. It has a rigid structure and does not swell in solvent, and can be used at both high and low temperatures and at high pressure.[7–10] SBA-15, a kind of inorganic mesoporous silica material with large specific surface area (690–1040 m^2/g), well-defined, tunable pore sizes (47–300 Å) and thick framework walls (31–64 Å)[11], provides a good opportunity for the immobilization of large catalytic species, and also for the promotion of catalytic conversions of bulky organic reactants.

The mesoporous silica SBA-15 was synthesized according to the literature using tri-block poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), $EO_{20}PO_{70}EO_{20}$, as a template in acidic conditions.[11] Before being functionalized with the Ru complex, the outer surface of SBA-15 was modified in advance with Si-



Scheme 2. Synthesis and immobilization of ruthenium carbene complexes.

CH_3 groups to prevent any deposition of the Ru complex on the outer surface, and afterwards the surfactant was removed by solvent extraction.[12] The synthesis and immobilization route to complex **7** is shown in Scheme 2. Ligand **6** (in Scheme 2) was readily prepared from commercially available imidazole by *N*-alkylation[13] with *n*-BuBr and 1-chloro-3-trimethoxysilylpropane, followed by the treatment with NaH in the presence of potassium *tert*-butoxide.[14] Complex **7** could be produced in high yield by reaction between **6** and Grubbs catalyst in THF solution.[15] Immobilization of complex **7** in the pore channels of SBA-15 was carried out through refluxing it with SBA-15 in *N,N*-dimethylformamide (DMF) solution under a nitrogen atmosphere.

The anchored ruthenium complex **7** in SBA-15 was confirmed by FT-IR. The IR spectra of SBA-15 were recorded before and after immobilization (Figure **1**). The peak at 960 cm^{-1} assigned as Si–OH stretching of the surface silanols almost disappeared after immobilization, meanwhile the characteristic peaks at 1498–1660 cm^{-1} and 750 cm^{-1}, which could be related to the C–C vibration of benzene and P–C vibration of PCy_3, respectively, appeared, indicating that complex **7** had been loaded onto the support.

After the immobilization the hexagonal pore structure of SBA-15 remained intact. Figure 2 shows an HR-TEM image of the sample after immobilization taken with the electron beam parallel to pore channels. The mesoporous channels are well ordered with a characteristic hexagonal structure as suggested by the electron diffraction pattern. The simultaneous EDS analysis, as showing in Figure 3, indicates that Ru element exists inside the pore channels of SBA-15. As the high surface area of SBA-15 material is mainly contributed by its open pore system and the outer surface of the material has been pre-coated with $Si–CH_3$ groups, therefore, all of the catalytic functional groups prepared *via* this

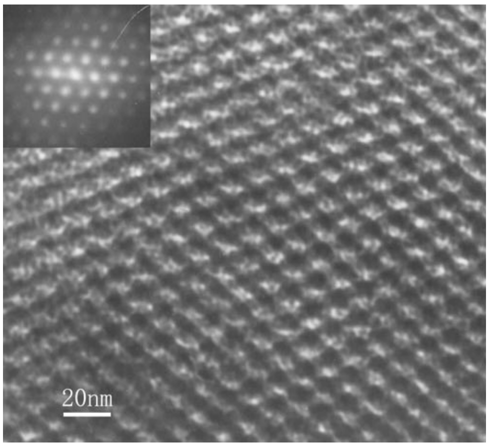


Figure 2. HR-TEM image of SBA-15 after immobilization.

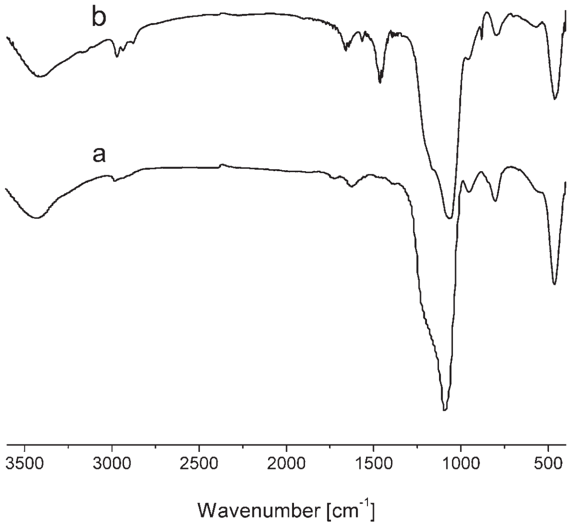


Figure 1. FT-IR spectra of SBA-15; **a**: before immobilization; **b**: after immobilization.

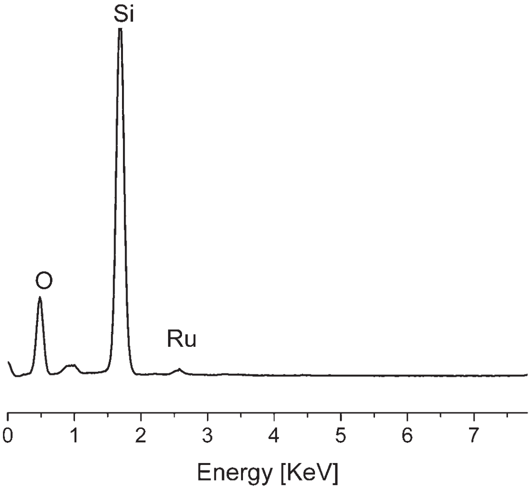


Figure 3. EDS spectra of Ru-SBA-15 after immobilization.

scheme, as we believe, should have been confined in the pore channels.

The N_2 adsorption/adsorption isotherms of these materials are shown in Figure 4. The type IV isotherm curves with a well defined step clearly indicate that these materials possess a mesoporous structure. After immobilization the BET surface area of SBA-15 decreased from 734 m^2/g to 233 m^2/g and the average pore size decreased from 7.4 nm to 5.2 nm due to the loading of the Ru complex in the mesoporous structure. However, the pore size was still large enough to permit the diffusion of large organic molecule in it.

The catalytic activity of **8** was tested through standard ring-closing metathesis (RCM) diallylmalonic acid diethyl ester (Scheme 3),[16] and the results are shown in Table 1. At 45 °C in CH_2Cl_2, the RCM product was almost equally formed after 35 min reaction for each cycle, and could be isolated as a colorless oil after filtration and concentration. The first cycle catalytic activity is very similar to the corresponding homogeneous catalyst (about 92% conversion after 25 min[9]), which means that the reaction is, most probably, not diffusion-controlled due to the high porosity of the SBA-15 material.

In order to test its recycle and reuse capability, after the first reaction, all the catalysts were separated by filtration and thoroughly washed, and then reused under the same conditions. The reaction conversion data (Table 1) show that the immobilized catalyst can be repeatedly used at high catalytic activity without any apparent decrease in catalytic activity along with the cycle times. For this heterogeneous catalyst, the catalytic species were covalently anchored on the inner surface of the pores in SBA-15, and it is very difficult, as we believe, for them to come to contact and react with each other, so the material exhibited a high catalytic activity even after being reused for several times. The element analysis by the ICP technique indicated that there was no Ru element in the reaction mixture within the detection limits. The immobilized catalyst showed very high stability against leaching of the active species into the liquid phase under the given reaction conditions. This feature, which is important for a heterogeneous catalyst system, is mainly ensured by the relatively strong interaction between the silane coupling agent and the Ru center and by the covalent grafting between the organic ligands and the inorganic mesoporous materials.

In Table 2 are listed the results of other metathesis reactions catalyzed by 5 mol % of supported catalyst **8** for 10 h. It shows that this immobilized catalyst has a high catalytic activity for olefin metathesis reactions.

Table 1. Recycling and reuse of the mesoporous silicon-bounded Ru complex in ring-closing metathesis of diallylmalonic acid diethyl ester.

Cycle	1	2	3	4	5
Conversion (35 min, %)	98	96	96	95	95

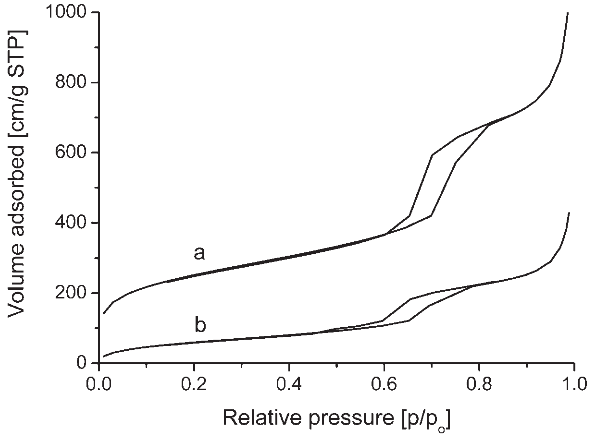
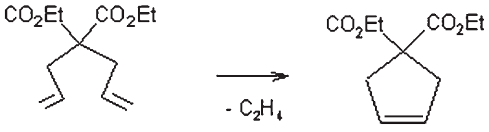
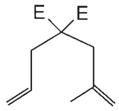
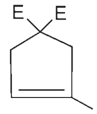
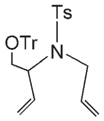
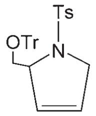
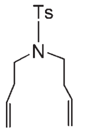
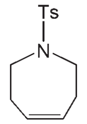
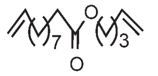
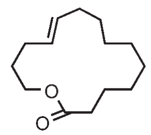


Figure 4. Nitrogen adsorption-desorption isotherms; **a**: before immobilization; **b**: after immobilization



Scheme 3. Ring-closing metathesis (RCM) reaction of diallylmalonic acid diethyl ester.

Table 2. Result of metathesis reactions utilizing the immobilized catalyst.[a]

Entry	Substrate	Product	Yield [%]
1			100
2			98
3			100
4			82

[a] All reactions have been performed under standard conditions employing 5 mol % of catalyst at 45 °C in CH_2Cl_2 for 10 h. E = ester group, Ts = *p*-toluenesulfonyl, Tr = triphenylmethyl.

In conclusion, through introducing Si–OMe groups to one of the ligands, the Ru carbene complex has been mainly covalently anchored on the inner pore surface of the inorganic mesoporous material SBA-15. After the immobilization, the decomposition of the catalytic species has been effectively prevented and durable catalytic activity has been achieved. This method can also be used for the immobilization of other heterogeneous metal complex catalysts.

Experimental Section

Modification SBA-15's Outer Surface with Si–CH_3 Groups

SBA-15 (1.5 g) was dispersed in dry toluene (50 mL) at 70 °C under a N_2 atmosphere, then $(CH_3)_3SiCl$ (10 mL) was added under stirring. The mixture was filtered after being continuously stirred for 24 h, followed by drying in vacuum at 90 °C for more than 8 h. After modification of the external surface, the surfactant template was removed by solvent extraction using refluxing ethane under stirring for 2 days.

Synthesis of 5

A 250-mL, round-bottom flask was charged with *N*-butylimidazole (9.7 g, 75 mmol), 31 g (75 mmol) of 1-chloro-3-trimethoxysilylpropane, a stir bar, and 100 mL of toluene. The mixture was stirred at 110 °C for about 12 h and then separated through a funnel, and the oil-like sample was washed with toluene (2 × 20 mL); Yield: 16.7 g (70%); anal. calcd. for $C_{13}H_{26}ClN_2O_3Si$: C 48.52, H 8.09, N 8.71; found: C 48.71, H 8.15, N 8.50%; ^{1}H NMR ($CDCl_3$): $\delta = 0.65$ (m, 2H, $SiCH_2$), 0.91 (t, 3H, CH_3CH_2), 1.35 (m, 2H, CH_3CH_2), 1.89 (m, 2H, $SiCH_2CH_2$), 2.05 (m, 2H, $CH_3CH_2CH_2$), 3.57 (s, 9H, OCH_3), 7.16 (t, 2H, $NCH_2CH_2CH_2Si$), 7.25 (t, 2H, $NCH_2CH_2CH_2CH_3$), 7.48,7.63 (s, 2H, NCHCHN).

Synthesis of 6

A 250-mL, round-bottom flask was charged with 1-butyl-3-trimethoxysilylpropylimidazolium chloride (10 g, 60.1 mmol), 2.05 g (85.4 mmol) of oil-free sodium hydride, a stir bar, and 100 mL of THF. The suspension was stirred for 3 min to insure good mixing, and 400 mg (3.6 mmol, 5 mol %) of potassium *tert*-butoxide in 10 mL of THF was added as a single portion. The flask was capped with a septum, and the rate of hydrogen evolution was monitored by piercing the septum with a hypodermic needle connected to an oil-filled bubbler. After 4 h the reaction mixture was filtered through Celite, and the filter cake was washed with THF (2 × 20 mL). The combined filtrate and washes were concentrated under vacuum to give a light yellow viscous liquid.

Synthesis of 7

A solution of $RuCl_2(=CHPh)(PCy_3)_2$ (0.606 mmol) in THF was treated with a solution of **5** (0.606 mmol) in THF (20 mL) at −78 °C and slowly warmed to room temperature. The solution was filtered and the solvent removed. The complex was washed with pentane (3 × 20 mL), and the resulting orange-brown solid was dried under vacuum; yield: 350 mg (70%); anal. calcd. for $C_{38}H_{65}Cl_2N_2O_3PSiRu$: C 54.41, H 7.96, N 3.43; found: C 54.53, H 7.92, N 3.32%; ^{1}H NMR ($CDCl_3$): $\delta = 0.82$ (m, 2H, $SiCH_2$), 1.28 (t, 3H, CH_3CH_2), 1.12–1.91(all m, 30H of PCy_3), 1.81 (m, 2H, CH_3CH_2), 1.89 (m, 2H, $SiCH_2CH_2$), 2.01 (m, 2H, $CH_3CH_2CH_2$), 2.38 (m, 3H, CH of PCy_3), 3.61 (s, 9H, OCH_3), 7.12 (t, 2H, $NCH_2CH_2CH_2Si$), 7.21 (t, 2H, $NCH_2CH_2CH_2CH_3$), 7.30–7.48 (m, 5H, C_6H_5), 7.70, 7.72 (all s, 1H, NCHCHN), 20.32 (s, 1H, Ru-CH); ^{31}P NMR ($CDCl_3$): $\delta = 34.88$ (s Ru-PCy_3).

Synthesis of 8

A solution of complex **7** (816 mg, 0.1 mmol) in dimethylformamide (DMF) (2 mL), was added to a well-stirred DMF suspension (40 mL) of the inorganic support (modified SBA-15 dried at 300 °C/0.1 mmHg for 3–4 h, 1 g) and the mixture was stirred at 130 °C under a nitrogen atmosphere for 24 h. The solid was then filtered and Soxhlet-extracted for 6 h to remove the remaining non-supported complex from the heterogenized catalyst.

Ring-Closing Metathesis

10 mmol of diallylmalonic acid diethyl ester were dissolved in 50 mL of CH_2Cl_2 and 1 mol % of the ruthenium complex was added. The suspension was stirred at 45 °C for the desired time. The results of the reaction was determined with GC-MS and ICP.

References

[1] T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29.
[2] M. R. Buchmesier, *New J. Chem.* **2004**, *28*, 549–557.
[3] S. T. Nguyen, R. H. Grubbs, *J. Organomet. Chem.* **1995**, *497*, 195–200.
[4] M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Lett.* **1999**, *40*, 8657–8662.
[5] S. C. Schurer, S. Gessler, N. Buschmann, S. Blechert, *Angew. Chem. Int. Ed.* **2000**, *39*, 3898–3901.
[6] M. Ulman, R. H. Grubbs, *J. Org. Chem.* **1999**, *64*, 7202–7207.
[7] M. Mayr, M. R. Buchmeiser, K. Wurst, *Adv. Synth. Catal.* **2002**, *344*, 712–719.
[8] J. O. Krause, S. Lubbad, O. Nuyken, M. R. Buchmeiser, *Adv. Synth. Catal.* **2003**, *345*, 996–1004.
[9] M. Chabanas, C. Copéret, J. M. Basset, *Chem. Eur. J.* **2003**, 971–975.

[10] J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2001**, *40*, 4251–4256.

[11] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.

[12] a) L. Li, J.-L. Shi, J.-N. Yan, *Chem. Commun.* **2004**, 1990–1991; b) L. Li, L.-X. Zhang, J.-L. Shi, J.-N. Yan, J. Liang, *Appl. Catal. A: Gen.* **2005**, *283*, 85–89; c) L. Li, J.-L. Shi, L.-X. Zhang, L.-M. Xiong, J.-N. Yan, *Adv. Mater.* **2004**, *16*, 1079–1082.

[13] a) M. R. Grimmett, *Imidazole and Benzimidazole Synthesis,* Academic Press, London, **1997**, p. 201; b) K. Sukata, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 280–284; c) T. Weskamp, V. P. W. Böhm, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12–22.

[14] a) A. J. Arduengo, H. V. Rasika Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534; b) A. J. Arduengo, H. V. Rasika Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[15] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.

[16] E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887–3891.