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Supported Ruthenium–Carbene Catalyst on Ionic Magnetic Nanoparticles for Olefin Metathesis

Shu-Wei Chen,[†,‡,§] Zhi-Cheng Zhang,[†,§] Miaofeng Ma,[†] Chong-Min Zhong,*[,†] and Sang-gi Lee*[,‡]

[†]College of Science, Northwest A&F University, Yangling, Shaanxi 712100, P.R. China

[‡]Department of Chemistry and Nano Science (BK Plus), Ewha Womans University, Seoul 120-750, Korea

Supporting Information

ABSTRACT: The Grubbs–Hoveyda ruthenium–carbene complex has been covalently immobilized on ionic magnetic nanoparticles utilizing an imidazolium salt linker. The supported catalyst exhibited excellent catalytic activity for ring-closing metathesis (RCM) and cross-metathesis (CM) in the presence of less than 1 mol % of ruthenium. The catalysts can easily be recovered magnetically and reused up to seven times with minimal leaching of ruthenium species.

Immobilization of homogeneous catalysts onto support materials is one of the primary strategies for developing cost-effective and environmentally benign catalytic systems that facilitate recovery and reuse of the catalyst.[1] Compatibility of the support material with the catalyst and/or reaction medium is one of the key factors influencing the stability, activity, and recyclability of the supported catalysts. Therefore, the search for new support materials and immobilization methods is of prime importance to the field of supported catalysis. Along these lines, we recently developed ionic nanomaterials via the covalent surface modification of silica nanoparticles and carbon nanotubes (CNTs) with ionic liquid moieties[2] for use as new supports. Notably, these CNTs with ionic liquid properties combine the key advantages inherent to both ionic liquids and nanomaterials, that is anion-directed tunable physiochemical properties of ionic liquids[3] and the high surface area of nanomaterials. The use of ionic nanomaterials functionalized with imidazolium salts facilitates the immobilization of palladium and gold nanoparticle catalysts with increased stability.[4] During our continuing study on the development of supported Ru-metathesis catalysts,[5] the Grubbs–Hoveyda Ru–carbene complex, one of the privileged metathesis catalysts, was also recently immobilized on ionic CNTs with excellent catalytic activity toward olefin metathesis.[5e,f] However, final recovery of the supported catalyst from the reaction mixture by the conventional methods of filtration or centrifugation is problematic. This challenge could be addressed by utilizing emergent magnetic nanoparticles (MNPs), which can easily be separated with the aid of an external magnet, to support the catalyst.[6] Herein, we report our recent efforts to immobilize the Grubbs–Hoveyda Ru–carbene complex on ionic magnetic nanoparticles (Ru@IMNPs **3**). These complexes exhibited excellent catalytic activity in ring-closing metathesis (RCM) and cross-metathesis (CM) reactions and were easily recyclable due to facile magnetic recovery.

Ruthenium-catalyzed olefin metathesis has become an indispensable method for the construction of carbon–carbon double bonds and is widely employed in a variety of chemistry fields, including natural product synthesis, pharmaceuticals, and polymer chemistry.[7] For greener and more cost-effective processes, significant effort has been deployed toward the development of supported Ru catalysts, particularly with Grubbs and Grubbs–Hoveyda catalysts on polymer, silica, ionic liquid, and per-fluorinated hydrocarbon support materials.[8] Although three examples of supported Grubbs–Hoveyda catalysts on MNPs have recently been reported,[9] the supported catalysts are still far from practical. Becasue of the significant leaching of the ruthenium species, many of the recyclability tests were investigated with a relatively larger amount of Ru catalyst (generally 2.5–5 mol %) compared to the standard homogeneous reaction, where less than 1 mol % of catalyst is high enough for olefin metathesis. Therefore, the development of a supported metathesis catalyst with high activity and good recyclability due to facile recovery is still an ongoing challenge.

Iron oxide (Fe_3O_4) MNPs were prepared according to the reported literature,[10] and their morphology was determined by transmission electron microscopy (TEM) displaying a relatively uniform composition with an average particle size of 230 nm (Figure 1a). The magnetic behavior of the MNPs was measured using a magnetic properties measurement system (MPMS-squid

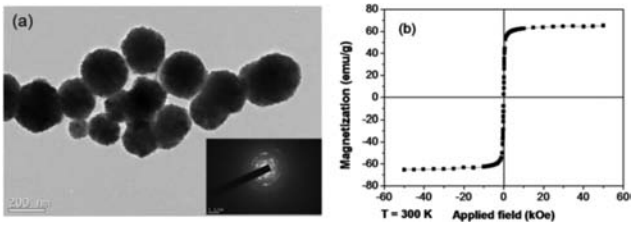

Figure 1. (a) TEM image and (b) magnetic hysteresis loop of MNPs measured at 300 K.

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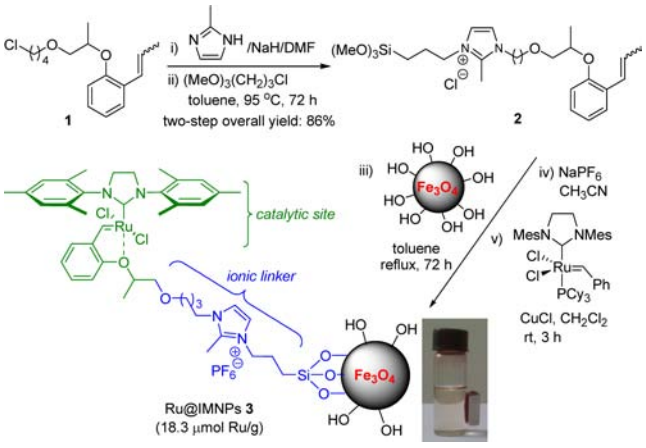
VSM-094) magnetometer. The saturation magnetization (M_s) value of the synthesized Fe_3O_4 was 65.3 emu g^{-1} at 300 K (Figure 1b). Infrared spectroscopy (IR) analysis clearly indicated the presence of hydroxyl groups on the MNP surfaces (see the Supporting Information). We anticipated that these hydroxyl groups could be a useful functionality with which to immobilize the catalyst.

The IMNP-supported Grubbs–Hoveyda type catalyst Ru@IMNPs **3** was prepared as shown in Scheme 1 (full details in the Supporting Information). The sequential reaction of the chlorinated ether **1**[5d] with 2-methyl-1*H*-imidazole and 3-chloropropyltriethoxysilane afforded the imidazolium chloride functionalized ligand **2**. Thermal grafting of ligand **2** onto the MNP surfaces, followed by anion exchange with $NaPF_6$ and metathesis with Grubbs' second-generation in the presence of CuCl, afforded the desired Ru@IMNPs **3** as a dark brown powder. ICP-MS analysis indicated that a loading amount of 18.3 μmol Ru/g (magnetic support) was achieved.

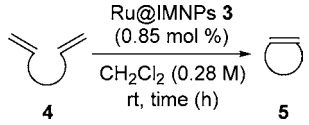
Scheme 1. Synthesis of Ru@IMNPs 3

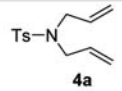
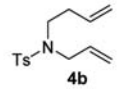
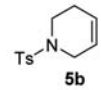
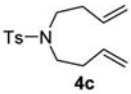
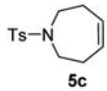
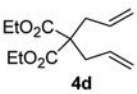
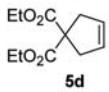
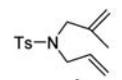
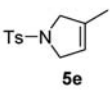
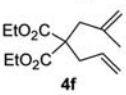
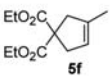
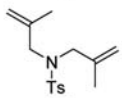
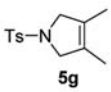


We first evaluated the catalytic activity of the supported Ru@IMNPs **3** in the RCM of dienes **4**, which have been frequently used as standard substrates to test the catalytic activity of supported metathesis catalysts. As shown in Table 1, RCM of terminal dienes **4a–d** were completed within 1 h (mostly within 0.5 h) at room temperature in the presence of only 0.85 mol % (based on Ru), affording the corresponding cyclic olefins **5a–d** (entries 1–4, Table 1). The RCM of dienes **4e** and **4f** providing trisubstituted olefins **5e** and **5f** were also completed at room temperature with a slightly prolonged reaction time (entries 5 and 6, Table 1). Moreover, the more sterically demanding diene **4g**, which is a notorious RCM substrate, cyclized smoothly at an elevated reaction temperature (90 °C in toluene). The supported Ru@IMNPs **3** also exhibited high CM catalytic activity in the reactions of methyl acrylate with 5-pentenylbezoate **6** and 3-phenyl-1-propene **7** providing the corresponding CM products **8** and **9**, respectively, in excellent yield and with *E*-selectivity (Scheme 2). The high catalytic activity of the ionic MNP-supported Ru catalyst, Ru@IMNPs **3**, was partly ascribed to the high compatibility of the ionic support with the reaction medium enhancing the rate of dissociation of the catalytically active Ru species.

After confirming the high catalytic activity, we next investigated the recyclability of the supported catalyst, Ru@IMNPs **3** for use in the RCM of **4a**. The suppported Ru@IMNPs **3** disperses well in methylene chloride to form a quasi-homogeneous brown solution, and upon completion of the reaction, it can be collected by applying an external magnet yielding a clear solution. After the supernant solution was decanted, the catalyst was washed three times with methylene chloride, and fresh solvent and substrate **4a** were added for the next run. As shown in Table 2, the catalytic activity was retained during the first six runs without significant loss of the catalytic activity. In the seventh run, however, the conversion rate was decreased resulting in only 76% conversion after 3 h. ICP-MS analysis clearly indicated significant leaching of the Ru into the product during the first three runs (ca. 130 ppm), which is equivalent to a loss of 54% of the initial Ru content. Nevertheless, it is worthy to note that although the leaching value is comparable to several other reported trace residual Ru values obtained from

Table 1. RCMs of Dienes with Ru@IMNPs 3[a]



entry	4	5	time (h)	conv[b] (%)
1	 4a	 5a	0.5	>99 (98)
2	 4b	 5b	0.5	>99 (98)
3	 4c	 5c	0.5	>99 (99)
4	 4d	 5d	1.0	>99 (98)
5	 4e	 5e	1.5	>99 (99)
6	 4f	 5f	6.0	97 (95)
7[c]	 4g	 5g	3.0	91 (90)

[a]Reactions were carried out with substrate (0.14 mmol, c = 0.28 M) and catalyst **3** (Ru = 0.85 mol %) at room temperature. [b]Determined by GC or ^{1}H NMR analysis; isolated yield after silica chromatography is shown in parentheses. [c]The reaction was carried out in toluene at 90 °C.

Scheme 2. CMs with Ru@IMNPs 3

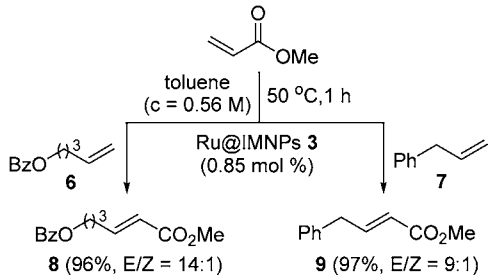


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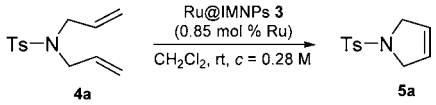
Table 2. Catalyst Recycling Experiments with Ru@IMNPs 3[a]



4a 5a

runs	1	2	3	4	5	6	7
time (h)	0.5	0.5	0.5	0.75	1.0	1.5	2
conv[b] (%)	>99	>99	98	98	96	96	76
Ru[c] (ppm)	50	49	32				

[a]Reactions were carried out with **4a** (0.14 mmol) at room temperature in CH_2Cl_2 (0.5 mL). [b]Determined by GC using mesitylene as an internal standard. [c]Residual Ru from the separated product determined by ICP-MS.

the product in metathesis with supported Ru-metathesis catalysts,[8] the recyclability of the Ru@IMNPs **3** was significantly improved. Even though there are still arguments regarding the release–return mechanism of Grubbs–Hoveyda-type catalysts,[11] this result suggested that, after leaching of Ru species, the molar ratio of chelating ligand attached to the ionic MNPs having reaction medium compatibility would become almost twice of the Ru species, which can be effectively recaptured.

In summary, the second-generation Grubbs–Hoveyda Ru–carbene catalyst was successfully immobilized on magnetically separable ionic magnetic nanoparticles having an imidazolium-based ionic liquid moiety as a linker. The supported Ru catalyst could effectively catalyze RCM and CM reactions in the presence of only 0.85 mol % Ru. In particular, the supported catalyst could easily be recovered by applying an external magnet and could be reused six times without significant loss of catalytic activity due to minimal leaching of Ru and high compatibility of the ionic support material with the reaction medium. Further studies on the surface modification of magnetic nanoparticles to increase the recyclability are currently underway and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization data for Ru@IMNPs **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhongcm@nwsuaf.edu.cn.
*E-mail: sanggi@ewha.ac.kr.

Author Contributions

[§]These authors contributed equally to this work

Notes

The authors declare no competing financial interest.

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