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# The effect of silica-coating on catalyst recyclability in ionic magnetic nanoparticle-supported Grubbs—Hoveyda catalysts for ring-closing metathesis

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#### 1. Introduction

Widely utilized in natural product synthesis, pharmaceutical research and development, and in polymer chemistry, rutheniumcatalyzed olefin metathesis has become indispensable for establishing the requisite carbon-carbon double bonds of target molecules.<sup>1</sup> To allow for greener and more cost-effective production by enabling the recovery and reuse of the catalysts, significant effort has been directed towards the development of supported catalysts by immobilizing the homogeneous catalysts and using a 'release and return' metathesis mechanism with the Grubbs-Hoveyda ruthenium catalyst.<sup>2</sup> During the last decade, various support materials such as polymers, silica, ionic liquids, and per-fluorinated hydrocarbons have been investigated as a means to immobilize these Ru-metathesis catalysts.<sup>3</sup> However, because of the significant leaching of the ruthenium species, many of the recyclability tests required a relatively larger amount of the ruthenium catalyst (generally 2.5-5.0 mol% compared to less than 1.0 mol% required for homogeneous reactions) limiting the practical application of these immobilized catalysts. Therefore, a supported metathesis catalyst with high activity and good recyclability due to facile recovery is still a challenging goal.

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#### ABSTRACT

The Grubbs—Hoveyda type ruthenium—carbene complexes have been covalently immobilized on both silica coated and uncoated magnetic nanoparticles utilizing an imidazolium salt linker. These MNP-supported catalysts showed comparable catalytic activity to the homogeneous imidazolium salt-tagged ruthenium catalyst in the ring-closing metathesis (RCM) of dienes, and could effectively catalyze RCM reactions in the presence of only 0.85 mol % Ru. The MNP-supported ruthenium catalysts could be easily recovered using an external magnet. The recyclability of the silica-coated MNP-supported catalysts allowing reuse 14 times, due to the increased compatibility of the silica-coated MNPs with the reaction medium.

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Compatibility issues regarding the interactions among the support material, the catalyst and the reaction medium is integral to the stability, activity, and recyclability of supported catalysts.

Therefore, it is important to the field of supported catalysis that new support materials and immobilization methods are developed. Accordingly, we recently developed ionic nanomaterials via the covalent surface modification of nanomaterials such as silica nanoparticles, carbon nanotubes (CNTs), and nanodiamonds with imidazolium salt-based ionic liquid moieties for use as new supports.<sup>4</sup> These ionic nanomaterials combine the important characteristics inherent to both ionic liquids and nanomaterials, i.e., the anion-directed tunable physiochemical properties of ionic liquids and the high surface area of nanomaterials.<sup>5</sup> In addition, the use of ionic nanomaterial functionalized imidazolium salts can facilitate the immobilization of palladium and gold nanoparticle catalysts with increased stability.<sup>6</sup> During our continuing studies directed towards the development of supported ruthenium-metathesis catalysts,<sup>7</sup> we recently immobilized Grubbs-Hoveyda Ru-carbene complex on imidazoliumа functionalized ionic CNTs with excellent catalytic activity toward olefin metathesis.<sup>7e,f</sup> However, the final recovery of the supported catalysts from the reaction mixture by the conventional methods of extraction, filtration or centrifugation was problematic. This challenge could be addressed by supporting the catalyst on the emergent magnetic nanoparticles (MNPs), which can be easily separated 2

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from the reaction mixture using an external magnet.<sup>8</sup> Despite the advantages of MNPs as support materials, only three recent examples of MNP-supported Ru-metathesis catalysts (**A-C**) have been reported (Fig. 1).<sup>9</sup>

isopropoxy group showed excellent catalytic activities for the RCM of dienes in ionic liquids.<sup>7d</sup> However, the recyclability of the catalysts was dependent largely on the tether length, the structure of the imidazolium tag and the ionic liquid, as well as the composition



Fig. 1. The MNP-supported Ru-metathesis catalysts.

The sugar-coated MNP-supported Grubbs-Hovevda catalyst A showed excellent catalytic activity, functioning with 0.05 mol % Ru and was reusable 5 times with minimal leaching of the Ru species (3.0 ppm) in the cross metathesis (CM) of methyl oleate.<sup>9a</sup> Although a relatively larger amount of the Ru-catalyst (2.5 mol %) was used, catalyst **B**, which is covalently immobilized on uncoated MNPs, can be reused up to 22 times in ring-closing metathesis (RCM) reactions.<sup>9b</sup> More recently, Robinson and co-workers also reported a new type of electrostatically immobilized MNP-supported Grubbs-Hoveydatype Ru-catalyst C, which catalyzed RCM reactions in the presence of 0.68 mol% of Ru and could be magnetically recovered and reused 5 times.<sup>9c</sup> However, due to the weak electrostatic interactions, significant amounts of the Ru species were leached out (ca. 519 ppm) decreasing catalytic activity upon reuse. This catalyst could be restored, however, by addition of the fresh Ru-carbene complex bearing a quaternary ammonium moiety. We envisioned that immobilization of the Grubbs-Hoveyda type Ru-carbene complex onto imidazolium salt-functionalized ionic MNPs could be useful as a new highly efficient MNPsupported metathesis catalyst with high recyclability. In a preliminary communication, it was found that the imidazolium saltfunctionalized ionic MNP-supported Grubbs-Hoveyda type Ru-carbene 1a, in which the surface hydroxyl group of the MNPs was used to anchor the trialkoxy silyl-functionalized chelating ligand, exhibited excellent catalytic activity in RCM and CM of olefins in the presence of 0.85 mol % of Ru, and the magnetically recovered catalyst could be reused 7 times.<sup>10</sup> Herein, we report the details and expand on our studies of silica-coated ionic MNP-supported Rumetathesis 1b, which significantly increased the recyclability of this catalyst in olefin metathesis allowing 14 times reuse.

#### 2. Results and discussion

## 2.1. Design, synthesis and characterization of MNP-supported Ru–carbene complexes 1a and 1b

Previously, we found that Grubbs–Hoveyda Ru–carbene complexes having an imidazolium salt tag attached to the chelating of the ionic solvent system. Thus, complex **2** with a 1.2-dimethyl imidazolium salt moiety and a long tether length showed superior recyclability to the catalysts in which the imidazolium salt had a 2-methine proton or was attached with a shorter tether length. On the basis of these observations, we anticipated that the MNPsupported Grubbs-Hoveyda Ru-carbene complexes 1 with the imidazolium salt tether that had been utilized for 2 could provide an effective recyclable metathesis catalyst. In order to compare the catalytic activity between homogeneous and supported catalysts, the imidazolium salt-functionalized Ru-carbene complex 2 was synthesized by the reaction of chlorinated ether 3, which can be readily prepared according to our previous protocol starting from commercially available 2-propenylphenol,<sup>7d</sup> with 1,2-dimethyl-1*H*imidazole, followed by anion exchange with NaPF<sub>6</sub>. For the immobilization of the imidazolium salt-functionalized Ru-carbene complex onto the MNPs, ligand 5 functionalized with trimethoxysilylpropyl imidazolium chloride was synthesized by the sequential reaction of chlorinated ether 3 with 2-methyl-1H-imidazole and 3-chloropropyltrimethoxysilane. Ligand 5 was then thermally grafted onto the surfaces of two different MNPs, silica-uncoated and silica-coated MNPs, which were prepared according to the reported procedures.<sup>11</sup> Anion exchange with NaPF<sub>6</sub>, followed by metathesis with Grubbs second-generation catalyst in the presence of CuCl afforded the desired MNP-supported Ru-carbene complexes 1a and 1b, respectively (Scheme 1). Inductively coupled plasma mass spectrometry (ICP-MS) analysis indicated that the Ru content (22.5 µmol/g) of silica-coated MNP-supported 1b was greater than that of silica-uncoated MNP-supported **1a** (18.3 µmol/ g). This difference is ascribed to the limited surface hydroxyl groups of the silica-uncoated MNPs. The X-ray photoelectron spectroscopy (XPS) analysis of **1b** also confirmed the anion exchange and successful immobilization of the Ru-carbene complex based on the observed binding energies at 686.3 eV for F1s, and at 463.2 eV and 485.8 eV for Ru3p(3/2) and Ru3p(1/2), respectively (Fig. 2). The morphology and magnetic behavior of the MNPs were measured by transmission electron microscopy (TEM) and a magnetic properties measurement system (MPMS-squid VSM-094) magnetometer before and after-silica coating. As shown in Fig. 3, the morphology of

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Scheme 1. Synthesis of ionic MNP-supported Ru-carbene complexes.



Fig. 2. XPS spectrum of 1b (right: Ru 3p and F 1s regions).

A: Before silica-coating



Fig. 3. TEM images and magnetisms for 1b: (A) before silica-coating (B) after silicacoating.

the MNPs was not significantly altered after silica-coating, and the magnetism was only slightly diminished.

#### 2.2. Catalytic activity and recyclability of MNP-supported 1a and 1b in RCM reactions

We first compared the catalytic activity of the MNP-supported Ru-carbene complexes 1a and 1b with the homogeneous Ru–carbene complex **2** in the RCM of *N*,*N*-bisallyl *p*-toluenesulfonamide **6a** in methylene chloride (Scheme 2). It has been found that all these catalysts exhibited extremely high catalytic activity. Moreover, the catalytic activity of the MNP-supported Ru-carbene complexes **1a** and **1b** is quite comparable with that of the homogeneous 2. Consequently, the RCM reactions with 1a and 1b went to completion within 30 min at room temperature in the presence of 0.85 mol % Ru-catalysts. We also compared the catalytic activity of 1a and 1b in the RCM of various dienes 6 that are frequently used as standard substrates to test the catalytic activity of supported metathesis catalysts. As shown in Table 1, the silica-coated MNP-supported catalyst **1b** showed higher catalytic activity than that of the uncoated MNP-supported 1a. For example, the RCM of dienes 6d and 6e with catalyst 1b was completed in shorter reaction times than when utilizing catalyst 1a (Table 1, entries 4 and 5). In addition, catalyst 1b enabled complete conversion of the RCM reactions of trisubstituted 6f and tetrasubstituted diene 6g, whereas the RCM with catalyst 1a did not go to completion (Table 1, entries 6 and 7).



Scheme 2. RCM with MNP-supported 1a, 1b, and homogeneous Ru-carbene complex 2.

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Table 1				
RCM of dienes wit	h MNP-supported	Ru-catalysts	1a and	1b

Entry	6	7	Cat	Time (h)	Conv (%) <sup>b</sup>
1	Ts-N 6a	Ts-N 7a	1a 1b	0.5 0.5	>99 >99
2	Ts <sup>-N</sup> 6b	Ts <sup>-N</sup> 7b	1a 1b	0.5 0.5	>99 >99
3	Ts-N 6c	Ts-N	1a 1b	0.5 0.5	>99 >99
4	EtO <sub>2</sub> C EtO <sub>2</sub> C 6d	EtO <sub>2</sub> C EtO <sub>2</sub> C 7d	1a 1b	1.0 0.5	>99 >99
5	Ts-N 6e	Ts-N 7e	1a 1b	1.5 1.0	>99 >99
6	EtO <sub>2</sub> C EtO <sub>2</sub> C 6f	EtO <sub>2</sub> C EtO <sub>2</sub> C 7f	1a 1b	6.0 4.0	97 >99
7 <sup>c</sup>	N Ts 6g	Ts-N	1a 1b	3.0 3.0	91 >99

<sup>a</sup> Reactions were carried out with substrate **6** (0.14 mmol, c=0.28 M) and catalyst **1** (Ru=0.85 mol %) at room temperature. The data for **1a** reported in reference 10 and used here for comparative purpose.

<sup>b</sup> Determined by GC or <sup>1</sup>H NMR analysis.

<sup>c</sup> Reactions were carried out in toluene at 90 °C.

After confirming the high catalytic activity of the MNPsupported Ru-catalysts 1a and 1b, we next compared the recyclability of these supported catalysts by using diene 6a. Both supported catalysts **1a** and **1b** dispersed well in methylene chloride to form a guasi-homogeneous brown solution, and, upon completion of the reaction, they could be collected by applying an external magnet yielding a clear solution (Fig. 4). After decanting the supernant solution, the catalyst was washed three times with methylene chloride, and fresh solvent and substrate 6a were added for the next run. As shown in Table 2, the silica-coated MNP-supported catalyst **1b** showed superior recyclability compared to the silica uncoated 1a, and thus, the catalytic activity of the recovered catalyst 1b was completely retained during the first 6 runs. Although the catalytic activity gradually decreased after the 7th run, the recovered catalyst could be reused a total of 14 times. ICP-MS analyses suggested that, although the effects were not significant, leaching of the Ru species into the product was influenced by the silica-coating: during the first three runs, ca. 130 ppm from 1a and *ca.* 101 ppm from **1b** were leached out. Even though there are still arguments regarding the release-return mechanism of Grubbs–Hoveyda type catalysts,<sup>2</sup> the observed higher catalytic



Fig. 4. Magnetic separation of MNP-supported catalyst 1.

activity and recyclability of the silica-coated MNP-supported catalyst **1b** suggested that the surface silicate may not only accelerate the dissociation of the Ru-complex, increasing the concentration of the catalytically active Ru-species, but may also increase the efficiency of its return to the stable complex via the chelating ligand attached to the surface of the silica-coated MNPs. The increased recyclability and decreased leaching of the Ru species of the silicacoated MNP-supported **1b** is ascribed to the grafting of an increased amount of the chelating ligand moiety onto the surface. In silicauncoated MNPs, there is a relatively smaller amount of hydroxyl functional groups that can be utilized for the grafting of trimethoxypropylimidazolium salt **5**.

#### 3. Conclusion

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 MNP-supported Ru-catalyst could effectively catalyze RCM reactions in the presence of only 0.85 mol % Ru. In particular, the silica-coated MNP-supported catalyst could easily be recovered by applying an external magnet and could be reused 14 times without significant loss of the catalytic activity due to the minimal leaching of Ru and high compatibility of the ionic support material with the reaction medium. These results suggest that the surface properties of the supporting material can significantly influence catalyst recyclability.

#### 4. Experimental section

#### 4.1. Materials and analysis

Dienes were synthesized and purified according to literature procedures.<sup>12</sup> The imidazolium salt-functionalized Ru–carbene **2** and chlorinated ether 3 were synthesized according to our previous methods.<sup>7d</sup> The MNPs were prepared according to the reported procedures<sup>13</sup> or purchased from Aladdin. Toluene was dried over sodium metal and distilled under argon. Dichloromethane was dried over calcium hydride and distilled under argon. All others chemical reagents and solvents were obtained from commercial sources and used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance spectrometers working at 500 MHz and 125 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. Gas chromatographic analyses were conducted on a Shimadzu GC-2014C equipped with a flame ionization detector. Mesitylene was used as an internal standard. High-resolution mass spectra (HRMS) were recorded on a Micromass TOF-Q II (Bruker) spectrometer. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis was carried out using an Agilent 725 ICp-OES or ICP-MS spectrometer (Agilent TeChnoLogies Corporation). Magnetic Properties Measurement System (MPMS) was measured with MPMS-squid VSM-094 magnetometer.

#### 4.2. Synthesis of MNP-supported 1a and 1b

4.2.1. 2-Methyl-1-{4-[2-(2-propenylphenoxy)-propoxy]-butyl}-1Himidazole (**4**). To a solution of NaH (0.44 g, 18.27 mmol, 60 wt% suspension in mineral oil, washed 3 times with anhydrous *n*-hexane) in anhydrous DMF (30 mL) was added 2-methyl-1H-imidazole (1.2 g, 14.61 mmol) at 0 °C. After stirring for 20 min at 0 °C, the (*E*)/ (*Z*)-mixture of chloride **3** (2.1 g, 7.31 mmol) was added, and then the mixture was stirred at room temperature for 12 h. After concentration under vacuum, the residue was purified by flash chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub>=2:25) to give **4** (2.1 g, 86.2%) as a yellowish oil. Spectral data of the major isomer: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (dd, *J*=7.8, 1.2 Hz, 1H), 7.18–7.11 (m, 1H),

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Cat.	Run	1	2	3	4	5	6	7	8-9	10	11	12	13	14
1a	Time (h)	0.5	0.5	0.5	0.75	1.0	1.5	2						
	Conv (%) <sup>b</sup>	>99	>99	98	98	96	96	76						
	Ru (ppm) <sup>c</sup>	50	49	32										
1b	Time (h)	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	1.0	1.0	1.0	24
	Conv (%) <sup>b</sup>	>99	>99	>99	>99	>99	>99	98	95	90	90	85	75	92
	Ru (ppm) <sup>c</sup>	69	19	13	11									

 Table 2

 Catalyst recycling experiments in the RCM of 6a with catalysts 1a and 1b<sup>a</sup>

<sup>a</sup> Reactions were carried out with **6a** (0.14 mmol) at room temperature in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The data for **1a** reported in reference 10 and used here for comparative purpose.

<sup>b</sup> Determined by GC using mesitylene as an internal standard.

<sup>c</sup> Residual Ru from the separated product determined by ICP-MS.

6.94–6.89 (m, 2H), 6.88 (d, *J*=1.1 Hz, 1H), 6.77 (d, *J*=1.1 Hz, 1H), 6.71 (dd, *J*=15.9, 1.6 Hz, 1H), 6.20 (dq, *J*=15.9, 6.6 Hz, 1H), 4.50 (sextet, *J*=4.9, 1H), 3.81 (t, *J*=7.3 Hz, 2H), 3.64–3.48 (m, 4H), 2.33 (s, 3H), 1.87 (dd, *J*=6.6, 1.6 Hz, 3H), 1.80–1.75 (m, 2H), 1.60–1.54 (m, 2H), 1.32 (d, *J*=6.2 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.8, 144.4, 130.4, 128.5, 127.7, 127.1, 126.5, 125.9, 121.3, 119.1, 114.8, 74.4, 74.3, 71.0, 46.0, 27.8, 26.9, 19.0, 17.4, 13.1 ppm; HRMS Calcd for C<sub>20</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub>: 329.2224. Found 329.2205.

4.2.2. 2-Methyl-1-{4-[2-(2-propenylphenoxy)-propoxy]-butyl}-3-(3trimethoxysilyl propyl)-1H-imidazolium chloride (5). To a solution of compound **4** (100 mg, 0.304 mmol) in anhydrous toluene (150 µL) was added 3-chloropropyltrimethoxysilane (121 mg, 0.608 mmol). The reaction mixture was stirred at 95 °C for 72 h. After cooling to room temperature, the mixture was dissolved in toluene (0.5 mL), washed with diethyl ether 4–5 times to remove impurities, and then dried under vacuum at 90 °C to give the desired compound 5 (158.6 mg, 99%) as a yellow solid. Spectral data of the major isomer: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (m, 1H), 7.51–7.03 (m, 3H), 6.89 (m, 2H), 6.69 (dd, J=15.9, 1.6 Hz, 1H), 6.20 (dq, J=15.9, 6.6 Hz, 1H), 4.53 (m, 1H), 4.35-4.23 (m, 4H), 3.57 (m, 13H), 2.66 (s, 3H), 1.90–1.82 (m, 7H), 1.64 (s, 2H), 1.29 (d, *J*=6.2 Hz, 3H), 0.74–0.65 (m, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  154.8, 143.1, 127.8, 126.4, 126.2, 125.8, 121.9, 121.6, 121.2, 114.6, 74.7, 74.3, 70.9, 50.8, 50.6, 48.7, 27.4, 26.1, 23.7, 19.1, 17.1, 10.2, 6.0 ppm.

4.2.3. Preparation of silica-coated MNPs. Iron oxide MNPs (0.8 g) were dispersed into 400 mL of 0.1 M aqueous HCl, and stirred vigorously for 10 min. The MNPs were separated with a magnet, washed with deionized water 3 times, and then homogeneously dispersed in a mixture of ethanol (640 mL), deionized water (160 mL) and aqueous ammonia (28 wt %, 8.0 mL). To this solution was added TEOS (0.8 g) at room temperature, and the mixture was vigorously stirred with a mechanical stirrer at 50 °C for 6 h. The product was separated with a magnet and washed with deionized water and ethanol 3 times before being dried under vacuum at 60 °C for 12 h.

4.2.4. Preparation of MNP-supported Ru–carbene complex **1b**. In a glove box, compound **5** (120 mg, 0.227 mmol), silica-coated MNPs (1.2 g), and anhydrous toluene (3.8 mL) were placed in a screwcapped reaction vial. The vial was moved out of the glove box, and the mixture was stirred at 135 °C for 72 h. After cooling to room temperature, the MNPs were separated with a magnet and washed with anhydrous acetonitrile 4 times. The separated MNPs were dried under vacuum at room temperature for 2 h. For anion exchange, a solution of MNPs (1.25 g) and NaPF<sub>6</sub> (67.18 mg, 0.4 mmol) in acetonitrile (4.0 mL) was stirred at room temperature for 12 h. The MNPs were separated again with a magnet and washed with anhydrous CH<sub>2</sub>Cl<sub>2</sub> 5 times. A solution of the anion-exchanged MNPs (0.5 g), Grubbs 2nd generation catalyst (33.96 mg, 40 µmol) and CuCl (7.92 mg, 80 µmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.8 mL) was stirred at room temperature for 3 h. After the reaction, the MNP-supported **1b** was separated with a magnet and washed with anhydrous  $CH_2Cl_2$  5 times before being dried under vacuum at room temperature for 1 h.

# **4.3.** A typical procedure for RCM using the MNP-supported Ru-catalyst 1b

A solution of diene **6a** (35.2 mg, 0.14 mmol) and MNP-supported catalyst **1b** (52 mg, Ru is 22.5  $\mu$ mol/g) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was stirred at room temperature until complete conversion was observed by GC. The catalyst was separated with a magnet and washed with anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5×2 mL). The combined CH<sub>2</sub>Cl<sub>2</sub> washings were evaporated and the residue was subjected to either GC or NMR analysis to determine the conversion. For catalyst recycling experiments, the magnetically separated MNP-supported catalyst **1b** was reused by the addition of fresh diene **6a** and solvent.

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