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Encapsulation of the Hoveyda–Grubbs 2nd generation catalyst in magnetically separable alginate/mesoporous carbon beads for olefin metathesis reactions in water†

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In this study, nano-sized mesoporous carbon-supported HG2 and magnetic γ -Fe₂O₃ nanoparticles were encapsulated within calcium alginate gels using a one-pot procedure. Mesoporous carbon within the hydrophilic alginate shell provided hydrophobic compartments for hydrophobic olefinic substrates to conduct olefin metathesis reactions in water under an air atmosphere. Stable alginate/mesoporous carbon gel structures were obtained in the presence of a non-ionic surfactant (Tween20) with a homogenous distribution of HG2 in the gel matrix as confirmed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The HG2 catalyst encapsulated in the alginate/mesoporous carbon matrix exhibited an improved performance in water, and quantitative yields were obtained in ring-closing metathesis reactions of diethyl diallylmalonate even in tap-water under the air atmosphere with no significant ruthenium and iron leaching. The catalyst can be easily separated from the reaction mixture with the aid of a magnet, and it can be reused up to 7 times in RCM reactions.

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Introduction

Olefin metathesis is a valuable and versatile tool for the construction of advanced molecular architectures in an efficient manner.¹ The discovery of ruthenium-based air and moisture stable Grubbs and Hoveyda–Grubbs catalysts have led to the development of diverse metathetic and non-metathetic transformation reactions in organic solvents.² Despite the air and moisture stability of Grubbs catalysts, adapting olefin metathesis reactions into water media is an ongoing challenge due to the hydrophobic nature of both olefinic substrates and Grubbs catalysts.³ To tackle these limitations, ionic and non-ionic hydrophilic group-tagged Grubbs catalysts were developed to improve the solubility of the catalysts in aqueous media.^{3–5} Grubbs catalysts were also immobilized on hydrophilic, hydrophobic and amphiphilic polymers, and biomolecules to conduct olefin metathesis reaction in water.⁶ The encapsulation of Grubbs-type

ruthenium catalysts in confined spaces emerges as a novel strategy for developing efficient metathesis catalyst systems with the improved performance, selectivity, and sustainability.⁷ The encapsulation strategy not only minimizes the catalyst leaching, but also isolates the hydrophobic spaces for various organic reactions, which are catalyzed by organometallic complexes in an aqueous medium.⁸ Several different materials including metal–organic frameworks, core/shell silica gels, polydimethylsiloxanes, directed organic ligands and amphiphilic polymers are utilized to encapsulate organometallic catalysts in hydrophobic confined spaces.⁹ As an example, Li *et al.* employed a post pore-size reduction strategy to encapsulate Hoveyda–Grubbs 2nd (HG2) generation catalysts within mesopores of silica gels.^{7a} Following this strategy, metal–organic frameworks have been employed to encapsulate Hoveyda–Grubbs type catalysts to increase their performance and stability within defined spaces.^{7d}

Recently, HG2 generation catalysts were immobilized in the cavity of β -cyclodextrin using a guest–host approach for aqueous ROMP reactions.¹⁰ Patel *et al.* encapsulated Grubbs 2nd generation (G2) catalysts in a calcium alginate gel matrix for ring-closing metathesis reactions (RCM) in aqueous media.¹¹ However, in the RCM reactions with bare G2/alginate catalysts in water, the covalent modifications of the alginate gel structure with an octyl group are necessary to improve the reaction rate of metathesis reactions due to the

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limited diffusion of hydrophobic substrates. These results point out that further isolated hydrophobic sites are required in the alginate gel structure for more efficient olefin metathesis reactions in aqueous media. In addition, alginate gels are also utilized along with supramolecular gels to obtain hybrid core/shell hydrogel beads for the Suzuki–Miyaura reactions that are catalyzed by *in situ* generated Pd(0) nanoparticles.¹²

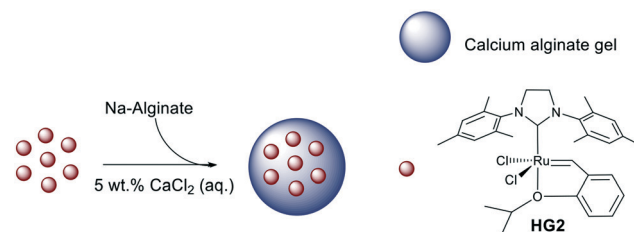
In this study, we have employed a facile strategy to form an alginate/mesoporous carbon-based metathesis catalyst through supporting the HG2 catalyst on nano-sized mesoporous carbon to create hydrophobic domains for olefin metathesis reactions in water. In addition, magnetic nano- γ -Fe₂O₃ was integrated into the calcium alginate gel structure to ease the catalyst separation after the metathesis reactions with the aid of a magnet. Moreover, quantitative yields were achieved in ring-closing metathesis reactions of diethyl diallylmalonate even in tap-water under the air atmosphere.

Results and discussion

The encapsulation of Hoveyda–Grubbs 2nd generation catalysts (HG2) in the alginate gel matrix is an efficient and straightforward strategy to integrate metathesis reactions into aqueous media. Although the ring-closing metathesis of hydrophobic substrates such as diethyl diallylmalonate (S1) runs smoothly in water with alginate-based metathesis catalysts, the presence of hydrophobic domains within alginate gel is required to obtain reasonable reaction rates.¹¹ Therefore, we have developed a novel hybrid material bearing nano-sized mesoporous carbon and nano- γ -Fe₂O₃ embedded in calcium alginate gel structure to obtain a robust and easily separable water-compatible olefin metathesis catalyst system. To assess the effects of hydrophobic domains within the alginate gel structure, a variety of alginate-based catalysts bearing HG2 was prepared in the presence and absence of mesoporous carbon.

Our first experiments were designed to directly encapsulate HG2 with calcium alginate beads. The particle size of HG2 in the solid phase was mechanically reduced prior to use. Briefly, HG2 was introduced into an aqueous 2 wt% sodium alginate solution in the solid phase and sonicated for approximately 30 minutes (alginate/HG2; wt/wt ratio: 10/1). After that, this solution was dropwise added to a 5 wt% CaCl₂ solution in water for generating sphere-like alginate beads. The greenish alginate beads were taken from the reaction mixture and dried under a high vacuum (Scheme 1).

The spherical alginate beads showed a non-uniform distribution of HG2 within the alginate matrix, as depicted by the visible dark green spots on the surface of the beads. Non-uniform regions can also be realized in scanning electron microscopy (SEM) images (Fig. 1). The region with different contrasts in the SEM images was analysed by elemental energy dispersive X-Ray analysis (EDX), and it was observed that the region mostly consisted of HG2 catalysts.



Scheme 1 Synthesis of the HG2@Alg catalyst.

In addition, these results suggest that a different approach is necessary for the homogenous distribution of HG2 in the alginate matrix instead of the solid-phase introduction of HG2. We envisaged that HG2 can be introduced into an alginate gel structure using a support material such as mesoporous carbon. The nano-sized mesoporous carbon as the support material can contribute to the homogenous distribution of HG2 in the alginate matrix. Furthermore, the hydrophobic nature of the mesoporous carbon will provide nano-sized isolated hydrophobic spaces to stabilize HG2 in water media. HG2 confined in the hydrophobic domains of mesoporous carbon would hurdle the diffusion limitations of hydrophobic substrates in water.

Although the alginate beads could be easily separated from the reaction mixture by simple filtration, the integration of magnetic materials such as nano-sized γ -Fe₂O₃ would ease the separation process, eliminating the need for the filtration process.¹³ Although the separation of metathesis catalysts from the reaction mixtures is a critical issue, only a few studies have been reported on the development of magnetically separable Hoveyda–Grubbs type catalysts.^{13,14} For instance, in an earlier report, Hoveyda–Grubbs type catalysts were immobilized directly on magnetic Fe₃O₄ or surface-functionalized Fe₃O₄ or Fe₂O₃ particles through covalent or ionic bonds.¹⁴ The direct encapsulation of nano-sized γ -Fe₂O₃ particles with alginate gels would eliminate the need for the covalent modification of the catalyst or support material surface. For this purpose, we have chosen γ -Fe₂O₃ as the magnetic particle and commercially available

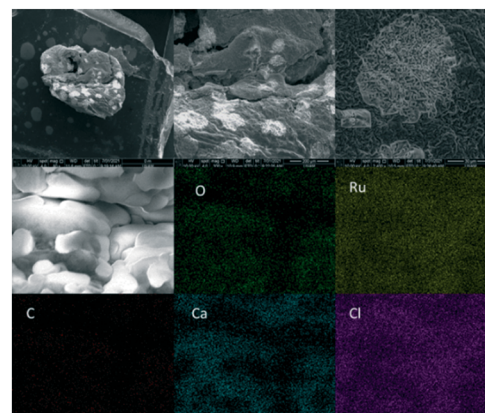
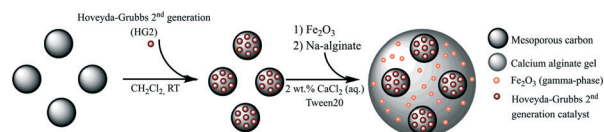


Fig. 1 SEM and elemental EDX mapping images of HG2@Alg.



Scheme 2 The synthesis of Alg@ γ -Fe₂O₃@HG2@MC.

mesoporous carbon (MC) as the most-suitable support material for HG2 in formulating the hybrid alginate gel structure. Mesoporous carbon was analyzed by means of high-resolution transmission electron microscopy (HR-TEM) and N₂ adsorption/desorption analysis prior to use in alginate gel structures. The images of the as-received mesoporous carbon exhibited the presence of spherical particles with average particle sizes of 50.9 ± 10.8 nm (ESI,† Fig. S1 and S2). Through the N₂ adsorption/desorption isotherms, the surface area of mesoporous carbon was calculated to be $206 \text{ m}^2 \text{ g}^{-1}$ with an average pore size of 4.00 nm and a pore volume of $0.66 \text{ cm}^3 \text{ g}^{-1}$ (Scheme 2).

HG2 was supported on mesoporous carbon using a simple protocol prior to the surfactant aided-alginate bead synthesis. In this regard, a Schlenk reactor was charged with HG2 (0.02 g, 0.032 mmol) in dichloromethane, and mesoporous carbon (0.10 g) was introduced to the reactor. Following this, the suspension was sonicated at 25 °C for 10 minutes, and then, the reaction mixture was magnetically stirred for 12 h at room temperature. Dichloromethane was removed under the high vacuum, and the isolated solid was washed several times with toluene and ethanol. The isolated HG2@MC was then used in encapsulation studies.

On the other hand, the encapsulation of HG2 that was supported on mesoporous carbon and magnetic γ -Fe₂O₃ nanoparticles with calcium alginate would lead to a novel hybrid gel system. The structural stability of calcium alginate gel is a critical issue to prevent the leaching of both ruthenium and γ -Fe₂O₃ nanoparticles during the metathesis reactions. First trials in the formula development stage were carried out using only mesoporous carbon, γ -Fe₂O₃, and sodium alginate solutions. These solutions were mixed in various ratios and then dropwise added to a calcium chloride solution to obtain the final gel structure (Table 1). In all cases, independent of the weight ratios of each substance in formulations, ring- or donut-shaped gel structures were

formed. These ring-shaped gels didn't exhibit physical stability and could not be isolated due to their physical structural integrity. The variations of the Alg/HG2@MC/ γ -Fe₂O₃ (wt/wt/wt) ratio did not improve the physical stability of the gels.

As reported in the literature, ionic and non-ionic surfactants could be used to stabilize the hydrophobic particles within the alginate matrix and could also contribute to the uniform distribution of hydrophobic substrates in an aqueous medium.¹⁵ Therefore, we tested cetyltrimethylammonium bromide (CTAB) as the cationic surfactant and Tween@20 and Synperonic®F108 as the non-ionic surfactants in alginate bead formulations, thereby improving the stability of alginate gels (Table 1 and Fig. 2).

The morphology of the ring-shaped alginate bead (Alg@ γ -Fe₂O₃@HG2@MC) was analyzed through the SEM study (Fig. 3). The SEM images show some cracks on the surface of the ring-shaped alginate bead, and further studies with SEM-EDX mapping analysis proved the homogenous distribution of ruthenium within the alginate matrix. The spherical alginate bead that was obtained using non-ionic surfactant (Tween@20 and Synperonic®F108, Table 2-entry 5–6) formulation exhibited exceptional structural and mechanical stability (Fig. 4). SEM analysis showed that the surface morphology of the alginate bead was uniform, and there were no cracks observed on the surface of the bead. EDX mapping analysis showed the uniform distribution of all elements within the alginate matrix.

The X-ray photoelectron spectroscopy (XPS) analysis survey of Alg@ γ -Fe₂O₃@HG2@MC was demonstrated in the Fig. 5. XPS analysis showed the presence of C 1s at 284.7 eV. The shoulder on the main peak at 286.3 eV corresponds to the C–O–C groups in the alginate structure. The presence of carbonyl groups (O–C=O) corresponds to the peak appearing at 288.7 eV. The binding energy (eV) of Ru 3d_{5/2} electrons overlaps with that of C 1s in the 280.2–280.7 eV region; therefore, Ru 3d_{3/2}, Ru 3p_{5/2} and Ru 3p_{3/2} can be used to identify ruthenium in XPS analysis.¹⁶ In a systematic XPS study, Grela *et al.* observed the unique XPS binding-energy peaks for HG2 catalysts at 280.75 eV for Ru 3d_{5/2} and 462 eV for Ru 3p_{3/2}.¹⁷

In our case, no peaks were observed in the line-XPS scan for Ru 3d_{3/2} and Ru 3p_{3/2} electrons, indicating the absence of

Table 1 Alg@ γ -Fe₂O₃@HG2@MC formulations

	Alg/HG2@MC/ γ -Fe ₂ O ₃ /surfactant (wt%)				Morph. ^a	Stability ^b
1	58.8	29.4	11.8	—	Ring	Low
2	45.5	45.5	9.0	—	Ring	Low
3	41.7	41.7	16.6	—	Ring	Low
4	42.6	10.6	4.2	42.6 (CTAB)	Ring	Moderate
5	42.6	10.6	4.2	42.6 (Synperonic)	Spherical	High
6	42.6	10.6	4.2	42.6 (Tween@20)	Spherical	High

^a Morphology. ^b Alginate beads (0.05 g) in water (5 mL) were taken to a glass Schlenk reactor equipped with a magnetic stirrer. The mixture is magnetically stirred at 400 rpm; at regular intervals, the samples are withdrawn from the reaction mixture and analyzed by ICP-MS for metal leaching. The structural integrity of the alginate beads was also visually checked.

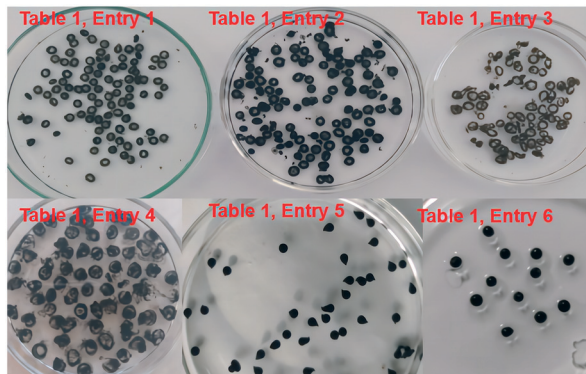


Fig. 2 Alginate beads were prepared with different formulations.

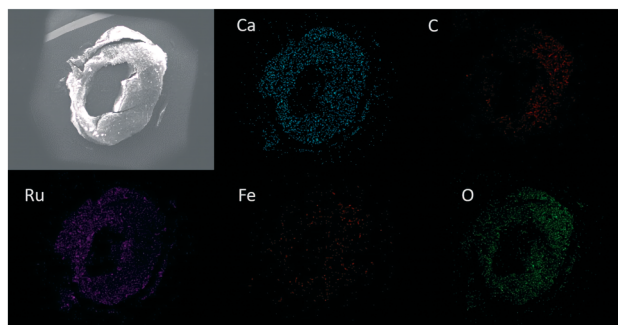


Fig. 3 SEM and elemental EDX mapping images of the ring-shaped alginate bead (Table 1, entry 4; Alg@ γ -Fe₂O₃@HG2@MC).

ruthenium at the outer shell of the alginate bead. Basically, the analysis of multilayered materials through the XPS analysis shows some limitations, including their capability to penetrate at the 10 nm depth-level from the surface, which is

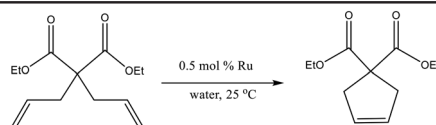
in great coherence with our observation.¹⁸ On the other hand, the electron dispersive X-ray (EDX) spectrum shows the presence of ruthenium at 2.59 keV. EDX analysis confirmed the presence of Fe (6.39 keV), Ca (3.69 keV), O (0.53 keV), and C (0.28 keV) within the alginate gel matrix (Fig. 6).

The thermogravimetric analysis (TGA) results of HG2@MC, Alg@ γ -Fe₂O₃@HG2@MC, and Alg@ γ -Fe₂O₃@MC were depicted in the Fig. 7a. No significant weight losses were observed between 50 °C and 290 °C at the given TGA profile of HG2@MC. Once the temperature was increased above 300 °C, a sharp weight loss was observed due to the thermal decomposition of HG2. A total weight loss of 28.8% was reached at 900 °C.

The weight loss in the region between 50–400 °C was more predominant due to the loss of absorbed water by alginate gel. The total weight loss was found to be 58.4 wt% for MC@HG2@Fe@Alg and 60.7 wt% for Alg@ γ -Fe₂O₃@MC. From these results, a significant amount of water was adsorbed by alginate beads, even though they were vacuum-dried at 25 °C overnight prior to analysis. Differential scanning calorimetry (DSC) analysis for alginate beads was demonstrate in the Fig. 7b. An endothermic peak at 97.86 °C and 99.14 °C was observed in both alginate beads, indicating the loss of the encapsulated water within the alginate structure. A sharp endothermic peak, appeared at 141.43 °C in the thermogram of Alg@ γ -Fe₂O₃@HG2@MC was related to the decomposition of the HG2 catalyst.

The FTIR spectra of HG2@MC and Alg@ γ -Fe₂O₃@HG2@MC were provided in the ESI.† The peaks appearing at 2925 and 2891 cm⁻¹ were related to the aliphatic C–H stretching. The symmetric stretching vibration peaks of the carboxylate group of alginate appeared at 1631 cm⁻¹. The asymmetric stretching of the same group appeared at 1456 cm⁻¹.

Table 2 RCM reactions of diethyl diallylmalonate (S1)



Entry ^a	Catalyst	Add.	Time (h)	Conv. ^c %	Yield ^d %	Ru leaching ^e (wt%)
1	HG2@MC	—	1	95	92	30
	HG2@MC	KCl ^b	1	98	95	32
2	HG2@Alg	—	24	74	70	0.1 × 10 ⁻¹
3	HG2@Alg	KCl	24	90	85	0.1 × 10 ⁻¹
4	Alg@HG2@MC	—	8	89	85	0.1 × 10 ⁻²
5	Alg@HG2@MC	KCl	5	99	98	0.1 × 10 ⁻²
6	Alg@HG2@MC	HCl ^b	5	99	98	0.1 × 10 ⁻²
7	Alg@ γ -Fe ₂ O ₃ @HG2@MC	—	8	90	85	0.1 × 10 ⁻²
8	Alg@ γ -Fe ₂ O ₃ @HG2@MC	KCl	5	99	95	0.1 × 10 ⁻²
9	Alg@ γ -Fe ₂ O ₃ @HG2@MC	HCl	5	99	95	0.1 × 10 ⁻²
10 ^f	HG2	—	4	75	70	n.d. ^g

^a All reactions were carried out in degassed pure water under a nitrogen atmosphere at 25 °C. ^b Aqueous 0.1 M HCl or KCl solution was used in the experiments. The mol/mol ratio of KCl/Ru or HCl/Ru is 10/1. ^c Determined by GC-MS using *n*-tetradecane as the internal standard. ^d Isolated yields. ^e Determined by ICP-MS analysis. ^f Diethylallyl malonate was dispersed in water (2 mL), and then HG2 (in solid-phase) was introduced into the solution. ^g Not determined.

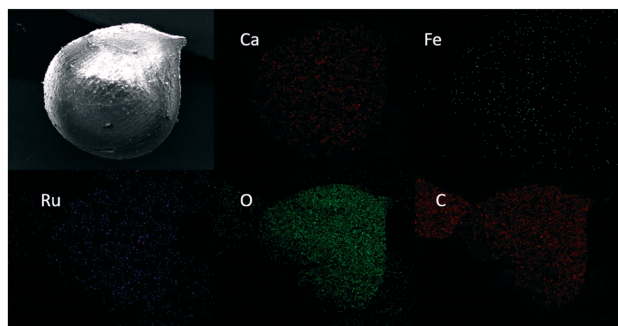


Fig. 4 SEM and elemental EDX mapping images of the ring-shaped alginate bead (Table 1, entry 4; Alg@ γ -Fe₂O₃@HG2@MC).

Catalysts that were prepared with different formulations such as HG2@MC, HG2@Alg and Alg@ γ -Fe₂O₃@HG2@MC were used in ring-closing metathesis (RCM) reactions to compare the effect of encapsulation on the activity of the catalyst (Table 2). First experiments showed that the reaction proceeded smoothly with a non-encapsulated catalyst (HG2@MC) and reached 95% conversion after 8 h of reaction time at room temperature in water in the presence of a catalyst loading (0.5 mol Ru %). These results were not surprising since in HG2@MC catalyzed RCM reaction, the substrate directly diffuses into the hydrophobic pore surface, providing the isolated sites for both HG2 and the hydrophobic olefinic substrate. However, a significant amount of catalyst leaching (up to 30 wt%) was observed in the first run. In the case of Alg@HG2 catalyzed RCM reactions, the rate of the reaction decreased significantly due to the diffusion limitations of the hydrophobic RCM substrate into hydrophilic alginate gel. The reaction reached 74% conversion after 24 h. As a result of efficient encapsulation of HG2 within the alginate matrix, only 0.01 wt% Ru leaching was observed in HG2@Alg catalyzed RCM reactions.

The hydrophobic compartmentalization effect of mesoporous carbon was systematically investigated in RCM of diethyl diallylmalonate using HG2@MC and HG2@Alg. As previously reported in the literature, the salt concentration

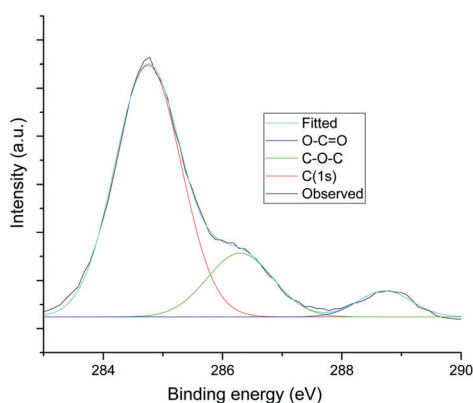


Fig. 5 XPS spectrum of Alg@ γ -Fe₂O₃@HG2@MC for C 1s.

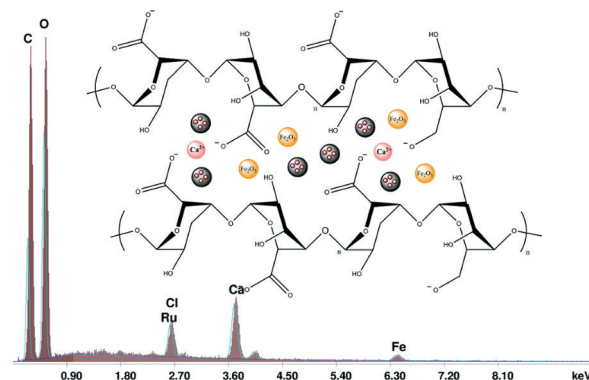


Fig. 6 EDX spectrum of Alg@ γ -Fe₂O₃@HG2@MC.

and pH have a positive impact on the metathesis reactions catalyzed by Grubbs-type catalysts in aqueous media.¹⁹ In this manner, Grubbs-type catalysts can undergo ligand exchange reactions in aqueous media, forming trace amounts of ruthenium-hydroxide species in water through the exchange of chloride ligands with hydroxide ligands. The addition of chlorine salts such as KCl prevents the formation of ruthenium hydroxide species, thus increasing the performance of the catalyst in water media. If HG2 is confined in hydrophobic domains in mesoporous carbon/alginate gel, the addition of KCl will not alter the performance of the catalyst. Accordingly, KCl addition did not improve the performance of both HG2@MC and HG2@Alg in the RCM of diethyl diallylmalonate. These results are not surprising since the pores of mesoporous carbon provide a perfect hydrophobic isolation site for HG2, thus preventing the formation of ruthenium hydroxide species. The first results confirmed that mesoporous carbon is a perfect support material for HG2 catalysts in aqueous media. Although HG2@MC showed superior performance in aqueous metathesis reactions, a significant amount of ruthenium leaching (up to 30 wt%) was observed in all cases. These results suggest that a hydrophilic shell material is needed to prevent catalyst leaching and required to increase the water compatibility of the catalytic system. Combining the advantages of both systems (HG2@MC and HG2@Alg), Alg@HG2@MC revealed a relatively high catalytic activity in RCM of DEDAM, reaching a conversion value of 89% within 8 h, and no Ru leaching was observed as confirmed by UV-vis and ICP-MS analyses. The addition of KCl and HCl improved

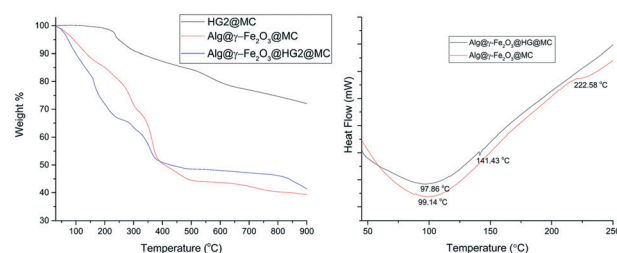
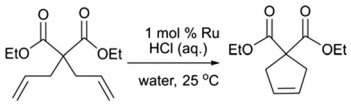


Fig. 7 TGA (a) and DSC (b) thermograms for various alginate beads.

Table 3 RCM reactions of diethyl diallylmalonate under harsh conditions

				
Entry ^a	Solvent	Atmosphere	Time (h)	Conv. ^b %
1	Deionized water ^b	N ₂ (g)	5	99
2	Deionized water	Air	5	98
3	Tap water (non-degassed)	N ₂ (g)	5	96
4	Tap water (non-degassed)	Air	5	95
5	Sea water (non-degassed)	Air	5	95

^a All reactions were carried out in degassed pure water under a nitrogen atmosphere at 25 °C. ^b Determined by GC-MS using *n*-tetradecane as the internal standard.

the reaction rate, giving conversion values up to 99% with a catalytic loading of 0.5 mol% Ru within 5 h of reaction time. On the next trial, the performance of magnetic γ -Fe₂O₃ integrated alginate bead catalysts (Alg@ γ -Fe₂O₃@HG2@MC) was investigated under optimized reaction conditions. The RCM reaction proceeded smoothly, and the reaction reached 99% conversion within 5 h in the presence of KCl and HCl. After the magnetic separation of the catalyst, the resulting aqueous solution was analyzed by ICP-MS to detect the possible leaching of iron and ruthenium during the metathesis reactions. The iron leaching was found to be only 0.01 wt%, and the ruthenium leaching was found to be only 0.001 wt% (10 ppm).

The air-compatibility of the catalytic system was tested on RCM of diethyl diallylmalonate by comparing the performance of the catalyst in deionized water and non-degassed tap water under an air and nitrogen atmosphere. As stated in the Table 3, quantitative conversion of the substrate was observed in all cases, and 95% conversion was obtained even under an air atmosphere using tap water.

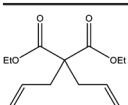
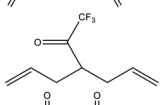
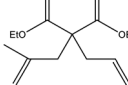
Once the optimum reaction conditions were determined, we have tested the different RCM substrates with different catalytic loadings, and the results were provided in the Table 4. The RCM reactions of *N,N*-diallyl-2,2-

trifluoroacetamide (S2) and diethyl-2-allyl-2-(2-methyl allyl) malonate (S3) were used as RCM substrates to expand the scope of the reaction. S2 was converted to the desired RCM product within 1 h of reaction time with a catalytic loading of 0.5 mol% Ru. S3, a sterically hindered substrate, was used in RCM reactions with a catalytic loading of 1 mol% Ru, yielding the corresponding RCM product in 75% conversion.

The leaching of the HG2 catalyst during the RCM reaction was investigated using filtrate tests. RCM of S1 (diethyl diallylmalonate) was initiated under predetermined reaction conditions with a catalytic loading of 1 mol% Ru. At 50% conversion of DEDAM, the catalyst was separated with the aid of a magnet, and the aqueous phase of the reaction mixture was separated into two parts. The first part remained in the reactor along with the catalyst, and the other part was taken to a different Schlenk reactor; both reactors were magnetically stirred at room temperature and analyzed at regular intervals by means of GC analysis.

The RCM reaction in the reaction mixture that was not in contact with the catalyst was stopped and reached to only 51% of conversion after 60 minutes. The other reaction mixture proceeded rapidly and reached to 99% of conversion after 60 minutes of reaction time. These results proved that

Table 4 RCM reactions of various dienes

Substrate ^a	Ru %	Time (h)	Conv. %
	5	1	99
	0.5	8	99
	0.1	24	55
	5	0.5	99
	0.5	1	99
	0.1	8	68
	5	6	90
	1	18	75

^a All reactions were carried out in degassed pure water in a nitrogen atmosphere at 25 °C under pre-determined reaction conditions that are given in the experimental section.

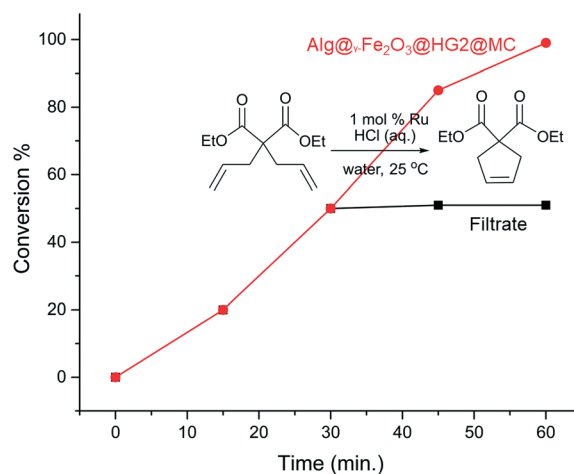
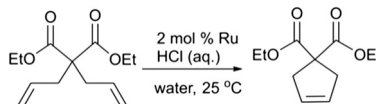
**Fig. 8** Filtrate tests for RCM reactions.

Table 5 The reusability tests of Alg@ γ -Fe₂O₃@HG2@MC catalyst

							
Cycle	1	2	3	4	5	6	7
Conversion (%)	99	94	90	80	75	55	25
Time (h)	1	1	1	2	12	24	48

the reaction proceeded in a heterogeneous manner; moreover, HG2 was not leached from the catalyst during the RCM reaction.

The reusability of the catalyst was tested with RCM of diethyl diallylmalonate with a catalytic loading of 2 mol% Ru in water media at 25 °C (Fig. 8). Once the conversion of diethyl diallylmalonate reached to a plateau, the catalyst was separated with the aid of a magnet. The aqueous layer was separated and extracted with diethyl ether to isolate the RCM product. The separated catalyst was washed with ethanol and water and then taken to the Schlenk reactor to initiate the second run (Table 5). During the first three runs, the performance of the catalyst didn't significantly change, and the corresponding RCM product was obtained in quantitative yields. The performance of the catalyst started to decrease after the fifth run due to the possible catalyst decomposition. At the 7th run, only 5% conversion was observed. The ICP-MS analysis of the catalyst after the 7th run indicated that only 2 wt% Ru was leached during the catalytic cycles, and the decrease in activity was due to the collapse of the gel structure. The SEM images of the used catalysts were demonstrated in the Fig. S10 and S11 (please see the ESI†). As it can be seen in the SEM images, the gel structure was collapsed after the 7th run which permitted the diffusion of the reactants. Although the RCM reaction was repeated at relatively higher temperatures, no improvement in reaction yield was observed. The decomposition of HG2 might be another issue for the activity loss after the 7th run.

Conclusion

Hoveyda-Grubbs 2nd generation catalysts supported on mesoporous carbon and magnetic γ -Fe₂O₃ nanoparticles were successfully encapsulated within calcium alginate gel to be employed as a novel water-compatible olefin metathesis catalyst system. The hydrophilic alginate gel acted as a perfect water-compatible shell material and minimized the catalyst leaching during metathesis reactions, thus enabling the synthesis of various RCM products in the aqueous medium. The RCM reactions of diethyl diallylmalonate were carried out in quantitative yields even under an air atmosphere using non-degassed tap or sea-water with a catalytic loading of 1% mol. The catalyst can be easily separated from the reaction mixture with the aid of a magnet and can be used up to 7 times in RCM of diethyl diallylmalonate.

Experimental section

Unless otherwise noted, all chemicals were purchased from Sigma-Aldrich and used as received. Sodium alginate (from brown algae, powder, viscosity ≥ 2000 cP for 2 wt% solution) was purchased from Sigma-Aldrich. Mesoporous carbon is dried in a vacuum oven overnight at 120 °C prior to use. The Hoveyda-Grubbs 2nd generation catalyst (HG2) was purchased from ABCR and stored under a nitrogen atmosphere. For direct encapsulation of HG2 in the alginate matrix, solid flakes were ground in a mortar to decrease the particle size in the solid-state. Nano-sized magnetic γ -Fe₂O₃ particles (average particle size 20–40 nm) were purchased from Alfa-Aesar and used as received.

X-ray photoelectron spectroscopy (XPS) analysis

The surface chemistry of the functionalized particles was analyzed with X-ray photoelectron spectroscopy (XPS) (K-Alpha XPS, Thermo Fisher Scientific, USA) to characterize the content. Basically, XPS determines the elemental composition and the chemical state in the material through the photoelectric effect under the ultra-high vacuum conditions ($\sim 10^{-9}$ – 10^{-7} mbar). XPS uses an argon ion gun to give photon energy to electrons. Photons are emitted from the top 1–10 nm layer of the material, and the electrons gain sufficient energy to escape into the vacuum chamber. We performed the XPS experiment by adding completely dried 100 mg powder samples to separate copper tapes which were attached to the XPS table. The samples attached onto the table were vacuumed for 30 minutes, and then the analysis was started after selecting specific points of the samples. After surveying the general elemental map of the composition, we finalized the experiment, particularly the XPS mapping of the specimens.

Environmental scanning electron microscopy (SEM) analysis

Environmental scanning electron microscopy (SEM) images were recorded using a FEI Quanta 200 FEG ESEM device. For the sample preparation, we first diluted the samples to 50 g L⁻¹ concentration values with the ethanol solvent. Then, the specimens were sonicated for 10 minutes, and we poured 2 μ L of them into (1 mm $\times$ 1 mm) silicon wafers. After drying the solutions, the wafers were attached to the stubs *via* slimy carbon tapes. The SEM images and Ametek EDAX energy dispersive X-ray (EDX) elemental maps of the specimens were

taken in a 20 Torr environment by selecting convenient voltage, magnification, and spot size values.

Synthesis of HG2@MC

A Schlenk reactor was charged with HG2 (0.02 g, 0.032 mmol) in dichloromethane, and mesoporous carbon (MC, 0.10 g) was added to the reactor; the resulting suspension was sonicated at 25 °C for 10 minutes. After that, the reaction mixture was magnetically stirred for 12 h at room temperature. Dichloromethane was removed under high vacuum, and the isolated solid was washed several times with toluene and ethanol. HG2 was loaded on mesoporous carbon as confirmed by ICP-MS analysis (0.244 mmol Ru per g).

Encapsulation of HG2 in calcium alginate gels (Alg@HG2)

HG2 (0.02 g, 0.032 mmol) in the solid phase was introduced in an aqueous sodium alginate solution (2.0 wt%, 10 g) and sonicated for 30 minutes under a nitrogen atmosphere. This solution was then dropwise added to an aqueous solution of calcium chloride (CaCl₂, 5 wt%). The solution was stirred for 24 h at room temperature to ensure the encapsulation of the catalyst. The alginate beads were then separated from the reaction mixture and dried in a vacuum oven.

Encapsulation of HG2@MC and γ -Fe₂O₃ in calcium alginate gels (Alg@ γ -Fe₂O₃@HG2@MC)

HG2@MC (0.2 g, 0.244 mmol Ru per g), γ -Fe₂O₃ (0.05 g), Tween@20 (0.8 g), and sodium alginate (2.0 wt% aqueous solution, 40 g) were mixed in a two-necked glass reactor and sonicated for 1 h under a nitrogen atmosphere. This solution was then added to an aqueous 5 wt% CaCl₂ solution dropwise to form spherical alginate beads. The alginate beads were gently stirred in CaCl₂ solution overnight and then solid alginate beads were separated and washed several times with deionized water (10 mL $\times$ 4) to remove the non-ionic surfactant. The alginate beads were washed with ethanol (10 mL $\times$ 2) and dried at room temperature for 12 h and then vacuum dried at 40 °C for 12 h. The final product was found to have a ruthenium content of 0.044 mmol Ru per g as confirmed by ICP-MS analysis.

Representative procedure for ring-closing metathesis reactions

A Schlenk reactor was charged with alginate beads (Alg@ γ -Fe₂O₃@HG2@MC, 0.10 g, 4.44 μ mol Ru) in 2 mL pure water, and then diethyl diallylmalonate (210 μ L, 0.87 mmol) was slowly introduced into the solution under constant stirring at room temperature. 1 M HCl(aq.) (45 μ L, HCl/Ru: 10/1; mol mol⁻¹) was then added to the reaction media. Aliquots (10 μ L) taken from the reaction mixture were extracted with dichloromethane (1 mL), dried over MgSO₄, and then, analyzed using the GC-MS. Once the reaction has reached the quantitative conversion values, the reaction mixture was filtered and then extracted with diethyl ether (5 mL $\times$ 2), and the organic phase was dried with

MgSO₄. Diethyl ether was evaporated, and the corresponding RCM product was isolated in quantitative yields.

Conflicts of interest

There are no conflicts to declare.

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