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Ammonium tagged Hoveyda–Grubbs catalyst immobilized on yolk/shell silica gels with a hydrophobic shell for olefin metathesis reactions†

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In this study, we have developed a novel yolk–shell silica material with a hydrophobic shell and a void interphase to encapsulate quaternary ammonium-tagged Hoveyda–Grubbs catalysts (Aquamet) for efficient ring-closing metathesis and ethenolysis reactions. This design facilitates the efficient diffusion of olefinic substrates into the catalyst core while simultaneously stabilizing ethylene gas within the hollow structure during the ethenolysis reactions. The hydrophobic characteristics of the outer layer improve the diffusion of hydrophobic substrates and serve as a moisture barrier, enhancing catalyst stability. The catalytic system has reached a turn-over number of 1000 for ethenolysis of methyl oleate at atmospheric pressure, yielding the corresponding ethenolysis products with 99% selectivity. The catalyst demonstrated excellent reusability, maintaining high efficiency up to the 8th cycle in ring-closing metathesis reactions of diethyl diallylmalonate with minimal catalyst loss of only 0.5 mol%.

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Introduction

Olefin metathesis is a powerful synthetic method that enables the efficient and selective construction of advanced molecular architectures.¹ A wide range of olefin metathesis catalysts, including those based on molybdenum, tungsten, and ruthenium, have been commercialized, largely due to the remarkable success of metathesis chemistry in both academic research and industrial applications. This success is especially attributed to the development of air-stable, functional group-tolerant catalysts, such as Grubbs and Hoveyda–Grubbs complexes.^{2–4} Over the past two decades, significant progress in catalyst design has expanded the scope of ruthenium-catalyzed metathesis reactions, encompassing both metathetic and non-metathetic transformations.⁴ Despite their high activity in homogeneous phase, the practical application of Grubbs-type catalysts at the industrial scale requires heterogenization strategies to allow for catalyst separation, recovery, and

reusability.^{5,6} Conventional approaches to catalyst immobilization involve covalent or ionic linkage between the metal complex and solid supports. However, these strategies often require chemical modifications to the ligand framework, which can lead to reduced catalytic efficiency relative to their homogeneous counterparts.^{7,8} To overcome these limitations, recent efforts have focused on physically encapsulating Hoveyda–Grubbs-type catalysts within confined environments—such as mesoporous silica, hollow silica, metal–organic frameworks (MOFs), self-assembled molecular cages, and biopolymers.^{9–13} This approach aims to merge the benefits of both homogeneous and heterogeneous catalysis, providing high selectivity, activity, and reusability. A common post-encapsulation strategy involves the silylation of pores using bulky organosilane derivatives to prevent catalyst leaching.^{9,14} However, this approach imposes significant steric hindrance, limiting substrate diffusion and reducing catalytic efficiency, particularly for sterically demanding substrates.

To address such diffusional limitations, core–shell and yolk–shell architectures have emerged as advanced support materials for catalyst encapsulation.¹⁵ These hierarchical structures allow for the immobilization of nanoparticles, metal complexes, and organic or inorganic molecules in confined spaces while enabling tuneable functionalization.¹⁶ For example, the encapsulation of zinc and copper oxides in SAPO-34 zeolite core–shell frameworks has been shown to enhance mass transfer and suppress side reactions during syngas-to-olefins conversion.¹⁷ Similarly, hybrid yolk–shell

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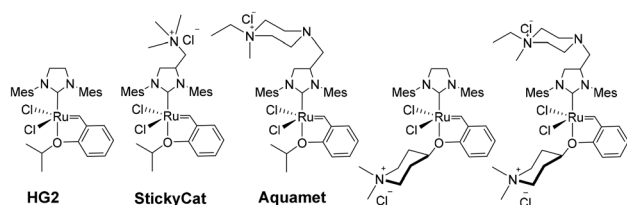
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structures with organic shells and inorganic cores offer enclosed voids for encapsulating metal nanoparticles such as Au, Pd, and Pt, improving catalytic efficiency in reactions like alcohol oxidation.¹⁸ In such systems, hydrophobic outer shells can facilitate the diffusion of hydrophobic reactants into the catalytic core, enhancing reactivity.¹⁹

Despite these promising developments, the encapsulation of ruthenium-based metathesis catalysts within yolk-shell architectures remains underexplored. Only a few studies have investigated the immobilization of Grubbs-type catalysts in such systems, particularly for challenging reactions like ethenolysis.¹⁰ For instance, the successful confinement of HG2 in silica-based yolk-shell particles—featuring an internal void between two SiO₂ layers—has demonstrated improved stability, especially when pore size was reduced post-synthesis using bulky silylating agents to prevent leaching.⁹ Nevertheless, optimal catalytic performance still depends on precise control of catalyst type, substrate size, and pore dimensions. To the best of our knowledge, no previous study has specifically employed yolk-shell materials bearing hydrophobic outer shells to encapsulate HG2-type catalysts. In this context, we designed a yolk-shell silica system featuring a hydrophobic outer layer and an interior void to improve the diffusion of olefinic substrates to the core, enhance ethylene gas stabilization, and protect the encapsulated catalyst from moisture. The presence of hydrophobic compartments and enlarged surface contact areas has been previously reported to enhance catalytic efficiency.²⁰ Furthermore, the hydrophobic outer layer acts as a protective barrier, minimizing moisture-induced catalyst degradation.²¹

In this study, the quaternary ammonium-tagged Hoveyda-Grubbs catalyst (Aquamet) was chosen as the metathesis catalyst for the immobilization onto the yolk/shell support material due to its high affinity for silica gel, robust catalytic performance, and excellent stability (Scheme 1).^{22–25} This design is intended to enhance catalytic efficiency by improving substrate diffusion, minimizing catalyst leaching, and protecting active sites from moisture-induced degradation. By evaluating the catalytic performance of this hybrid system in the ring-closing metathesis (RCM) of diethyl diallylmalonate and the ethenolysis of methyl oleate (MO) under atmospheric pressure. The proposed approach not only addresses existing limitations in catalyst heterogenization but also opens new avenues for valorising renewable feedstocks within the framework of green chemistry and industrial catalysis.



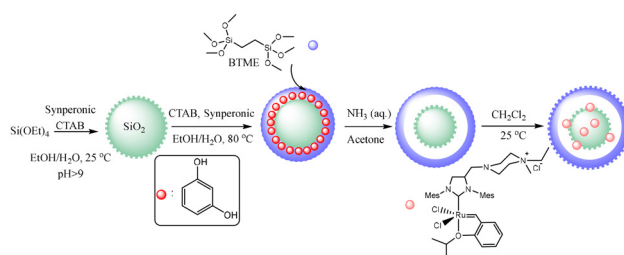
Scheme 1 Hoveyda–Grubbs type ruthenium metathesis catalysts.

Results and discussion

In this study, the yolk-shell system is based on the presence of a nano-sized silica gel (SiO₂), followed by a void space and a thin hydrophobic shell to confine ammonium-tagged Hoveyda-Grubbs catalyst within the core-void space to improve the contact time of olefinic substrates; especially ethylene, with catalyst (Scheme 2). For this purpose, nano-sized core silica gels were synthesized using a modified version of Stöber method using tetraethoxyorthosilicate (TEOS) as the silica source. Non-ionic surfactant; Synperonic®F108 and cationic surfactant; cetyltrimethyl ammonium bromide (CTAB) were dissolved in an ethanol/water mixture (v/v: 9/1) at room temperature. Concentrated aqueous ammonia solution was added to the reaction media, followed by drop-wise addition of TEOS. The TEOS amount was varied to tune the size of the silica gel. The spherical silica gel particles with an average particle size of 134.2 nm were denoted as SiO₂(1) (Fig. 1a and b) while silica particles with an average particle size of 51.8 nm (Fig. 1c and d) were denoted as SiO₂(2). The particle sizes are confirmed by TEM analysis (Fig. 1a–d).

On the next trial, hollow yolk/shell silica structures were prepared using a templating approach. For this purpose, two different mixtures, A and B, were prepared. For mixture A, non-ionic surfactant; Synperonic®F108, cationic surfactant; cetyltrimethyl ammoniumbromide (CTAB) and resorcinol; as the template molecule, were dispersed in ethanol/water mixture (v/v: 2/1) at room temperature and stirred at 280 rpm for two hours.

Mixture B was prepared through dispersing nano-sized silica gel (SiO₂(1) or SiO₂(2)) in 18 ml of deionized water, followed by sonification for 20 minutes. Mixture B was then poured into the mixture A and stirred at 80 °C for 24 h under constant magnetic stirring at 280 rpm. After 24 h, the coated silica gels were separated from the reaction mixture with centrifugation. To remove the surfactants and open the pore structures, the coated particles were refluxed in EtOH/HCl mixture for 24 h and then washed with water until a neutral pH was observed. A porous shell was formed around the core particle and the particle size was significantly increased as a result of coating the inner SiO₂ core with a hydrophobic shell using BTME as the hydrophobic silica precursor. As can be seen in TEM images of non-etch BTME@SiO₂, the porous outer shell contains residual surfactant and resorcinol. Therefore, the void between the core and shell is indistinguishable at this



Scheme 2 Synthesis of yolk-shell silica gel.

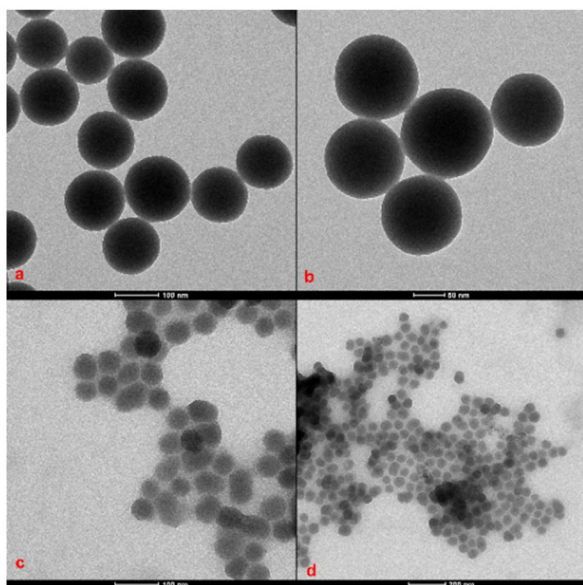


Fig. 1 High-contrast TEM images of nano-SiO₂ cores with different sizes (a and b) SiO₂(1); (c and d) SiO₂(2).

stage. To form a distinct void layer between core and the silica gel, the residual surfactants and template molecule resorcinol should be removed and the size of the inner core should be reduced through etching process. Following the stirring the non-etch BTME@SiO₂ with acetone/NH₃ mixture, a distinct void space was formed upon etching of the inner core and removal of templating molecules using NH₃/acetone mixture. The above process was repeated using two different silica gel cores, SiO₂(1) and SiO₂(2), to observe the effect of core size on the overall dimensions of the core-shell materials and the void space between the core and the shell. The core/shell material prepared by different silica gels is denoted as etch-BTME@SiO₂(1) and etch-BTME@SiO₂(2).

The average shell size was measured as 18.3 (±3.2) nm and the inner core size was measured as 126.0 (±14.1) nm as confirmed by TEM analysis for etch-BTME@SiO₂(1) with a relatively larger inner core (Fig. 2). The void distance is different in

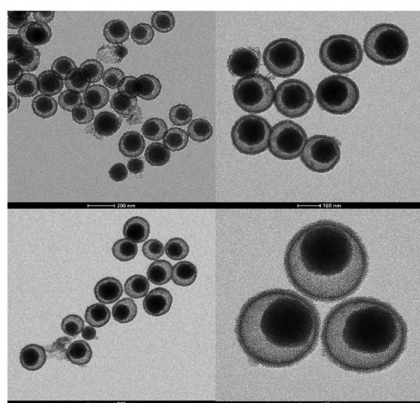


Fig. 2 High contrast TEM images of etch-BTME@SiO₂(1).

all particles however the average void distance between the core and the shell was measured as 42.4 nm. The overall size of the silica gel was determined as 179.8 nm. On the other hand, the core-shell particle with a relatively smaller silica core; etch-BTME@SiO₂(2), formed a narrow void layer between the core and the shell (Fig. 3). The average particle size and shell thickness were measured as 55.7 nm and 5.8 nm. The void space is very small when compared to the etch-BTME@SiO₂(1). The surface area of both core/shell silica particles were determined using N₂ adsorption/desorption isotherms. The surface areas are measured as 482 m² g⁻¹ for etch-BTME@SiO₂(1) and 349 m² g⁻¹ for etch-BTME@SiO₂(2). N₂ adsorption/desorption isotherms indicate a Type-IV isotherm for both particles with a hysteresis loop with delayed capillary evaporation between 0.55–0.99 and 0.38–0.99 relative pressure region (Fig. 4). Etch-BTME@SiO₂(1) was chosen as the support material for Aquamet immobilization and further catalytic reactions due to its high surface area and more distinct void space. Quaternary ammonium tagged Hoveyda-Grubbs analog (Aquamet) was chosen as the metathesis catalyst owing to its affinity to silica gel and robustness under

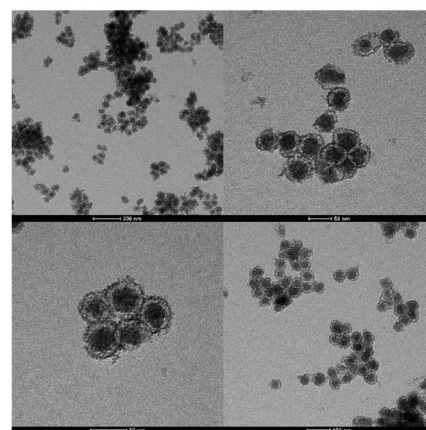


Fig. 3 High contrast TEM images of etch-BTME@SiO₂(2).

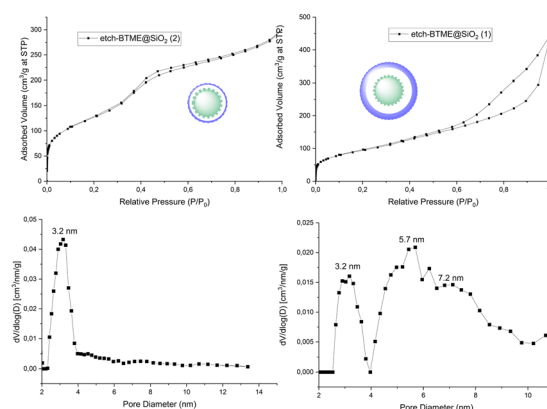


Fig. 4 N₂ adsorption/desorption isotherms and pore-size distribution of etch-BTME@SiO₂ yolk-shell materials.

harsh reaction conditions. A Schlenk reactor was charged with etch-BTME@SiO₂(1) (100 mg), Aquamet (1 wt% relative to support) and dry dichloromethane and stirred at room temperature for two hours under a nitrogen atmosphere. The organic solvent was removed by vacuum and the remaining solid was washed with dichloromethane/toluene and then dried under high vacuum overnight. The catalyst was denoted as Ru@etch-BTME@SiO₂(1). High-contrast TEM analysis and EDS mapping showed the uniform distribution of ruthenium around the inner core and void space of the core/shell material (Fig. 5). TEM-EDS line analysis of Ru@etch-BTME@SiO₂(1) showed two regions with different. The confinement of ruthenium complex was also evident with elemental line analysis (ESI, Fig. S12†).

Following the immobilization of Aquamet on etch-BTME@SiO₂, a green solid was observed following drying the sample under vacuum at 25 °C. Although the catalyst retains its stability at 4 °C for one week, the catalyst turned grey after one month of storage. The decomposition of the catalyst may arise from residual ammonia, which could trigger the first-order degradation of Grubbs and Hoveyda–Grubbs type complexes.²⁶ Similar cases are reported by Grela *et al.* when quaternary ammonium tagged Hoveyda–Grubbs complexes were supported on amine-functionalized metal–organic framework.²⁷ Therefore, the support material was washed with HCl in diethyl ether before immobilization and then the support material was dried under high vacuum. This strategy prevented the decomposition of the catalyst. The performance of the treated and untreated catalysts on long-term storage conditions is tested on ring-closing metathesis (RCM) of diethyl diallylmalonate (Table 1). As can be seen in Table 1, the acid treated silica gel retained its activity after one week of storage time. To demonstrate the effect of hydrophobic outer shell on performance of the catalyst, Aquamet was both supported on nano-sized silica gel (Ru@SiO₂) and core/shell material (Ru@etch-BTME@SiO₂(1)). In the first trials, the performance of the catalysts was tested on ring-closing metathesis (RCM) of diethyl diallylmalonate (DEDAM). As can be seen in Fig. 6, the performance of both catalysts showed similar performance, thus eliminating any diffusion limitation exerted by the outer shell of Ru@etch-BTME@SiO₂.

Although direct diffusion studies were not performed, the enhanced catalytic performance is consistent with previous reports in which hydrophobic shell architectures facilitated improved access of non-polar substrates to the catalytic core.¹⁹ Therefore, we propose that the hydrophobic outer layer in our system may play a similar role which improves the diffusion of

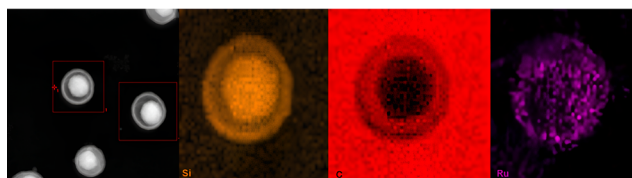
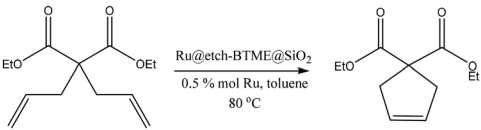


Fig. 5 TEM-EDX mapping of Ru@etch-BTME@SiO₂(1).

Table 1 The effect of pre-acid treatment of catalyst on the performance of RCM of diethyl diallylmalonate silica contents for shell and core of the particle

			
	Storage conditions	Storage time ^b	Conv. ^a %
Non-treated	N ₂ atmosphere	1 day	99
		1 week	67
	Air atmosphere	1 day	99
		1 week	45
	Vacuum	1 day	99
		1 week	72
HCl treated	N ₂ atmosphere	1 day	99
		1 week	99
	Air atmosphere	1 day	99
		1 week	95
	Vacuum	1 day	99
		1 week	99

^a Determined by GC-MS using *n*-tetradecane as internal standard.

^b Refers to the storage time of catalyst (Ru@etch-BTME@SiO₂(1)).

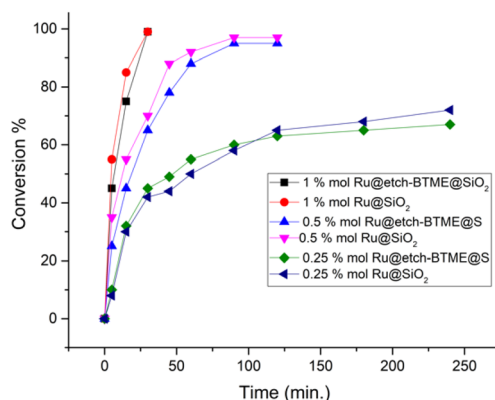
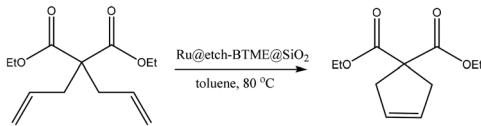


Fig. 6 RCM of diethyl diallylmalonate in the presence of core/shell catalyst (Ru@etch-BTME@SiO₂) and Ru@SiO₂ with different loadings.

olefins to the inner core. Also, comparable reaction rates are obtained when Aquamet is supported on both simple silica gel core (Ru@SiO₂) and core/shell silica gel (Ru@etch-BTME@SiO₂). To evaluate catalytic efficiency at lower ruthenium loadings, the RCM reactions were repeated under identical reaction conditions and the corresponding results are summarized in Table 2. As can be seen in Table 2, extension of reaction time is required to have reasonable reaction rates and TON values with 0.10 and 0.05 mol% Ru loadings using Ru@etch-BTME@SiO₂.

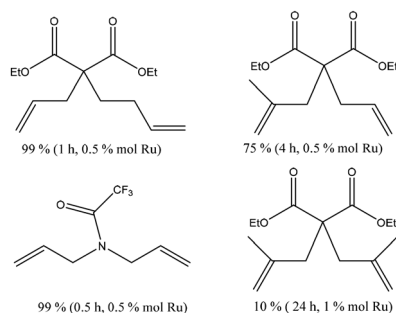
The performance of the catalyst was also tested on different dienes with varying steric hindrances and results are given in Scheme 3.

The performance of the yolk-shell catalyst was compared on RCM of diethyl diallylmalonate with other catalyst systems

Table 2 RCM of diethyl diallylmalonate with different catalytic loadings of Ru@etch-BTME@SiO₂


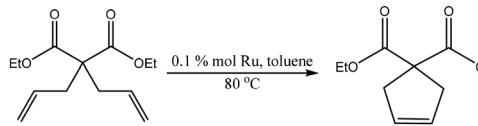
Entry ^a	Ru % (mol %)	Conv. ^b %	Time ^c	TON
1	1	99	0.5	99
2	0.5	95	2	190
3	0.25	67	4	268
4	0.25	90	10	360
5	0.10	38	2	380
6	0.10	88	12	880
7	0.05	29	12	580
8	0.05	60	24	1200

^a RCM reactions of diethyl diallylmalonate (0.1 M in toluene) were carried out in Schlenk reactors with a catalytic loading of 0.05–1 mol% Ru at 80 °C under a nitrogen atmosphere. ^b Determined by GC-MS using *n*-tetradecane as internal standard. ^c Represents the time when conversion of diethyl diallyl malonate has reached a plateau.

**Scheme 3** RCM of various dienes using Ru@etch-BTME@SiO₂.

bearing immobilized Aquamet catalyst (Ru) on various support materials (Table 3). The RCM of diethyl diallylmalonate (0.1 M in toluene) was carried out with a Ru loading of 0.1% in toluene at 80 °C. For comparison, Aquamet was immobilized on commercial silica gel (0.040–0.063 mm, average pore size: 6 nm, surface area: 500 m² g⁻¹), mesoporous carbon (50–100 nm, average pore size: 6.4 nm, surface area: 250 m² g⁻¹), SBA-15 (1–4 μm, average pore size: 6–11 nm, surface area: 550 m² g⁻¹) and magnetic core/shell mesoporous silica gel (410–430 nm, average pore size: 2.9 nm, surface area: 650 m² g⁻¹).^{23c,28} Yolk-shell catalytic system (Ru@etch-BTME@SiO₂(1)) showed comparable activity with Aquamet immobilized on SBA-15. In addition to direct experimental comparison, a literature comparison was also given in ESI† section.

On the next trial, the catalyst's performance was tested on ethenolysis of methyl oleate; a representative substrate for fatty acid methyl ester. Cross-metathesis and ethenolysis of fatty acid methyl esters (FAMES) provide efficient and highly selective pathways for the synthesis of a wide range of olefinic products.^{29,30} For economically viable ethenolysis with homo-

Table 3 The experimental comparison of various catalysts for RCM of diethyl diallylmalonate


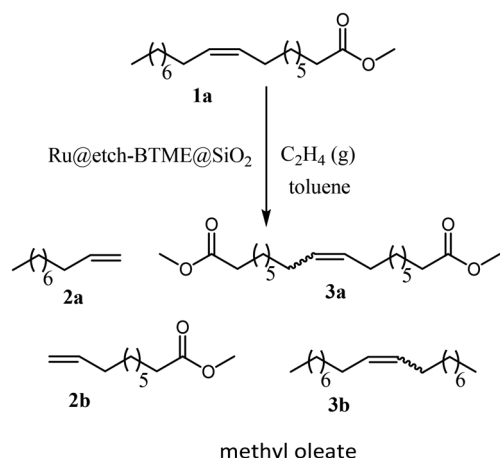
Catalyst ^a	Conv. ^b %	Time ^c (h)	TON
Ru (Aquamet)	50	4	500
Ru@SiO ₂ (commercial silica)	55	4	550
Ru@SiO ₂ (2)@Fe ₂ O ₃	75	9	750
Ru@Mesoporous carbon	80	2	800
Ru@SBA-15	90	2	900
Ru@etch-BTME@SiO ₂	88	12	880

^a RCM reactions of diethyl diallylmalonate (0.1 M in toluene) were carried out in Schlenk reactors with a catalytic loading of 0.1 mol% Ru at 80 °C under a nitrogen atmosphere. ^b Determined by GC-MS using *n*-tetradecane as internal standard. ^c Represents the time when conversion of diethyl diallylmalonate has reached a plateau.

geneous catalysts, turnover numbers (TONs) must exceed 50 000, as highlighted by DOW Chemical Company.³¹ In earlier examples, Grubbs' first-generation catalyst achieved TONs of 24 000 and 3284 under varying ethylene gas pressures and purity. Recently, Hoveyda–Grubbs analogs bearing cyclic alkyl amino carbene (CAAC) ligands have shown exceptional efficiency, achieving TONs of up to 740 000 with high substrate purity.^{32,33}

Encapsulation of HG2 catalysts in hollow silica gels of different morphologies (e.g., peanut, square, capsule) has demonstrated enhanced performance and selectivity at atmospheric pressure, facilitated by improved ethylene gas diffusion.¹⁰ Microfluidic systems further illustrate the impact of increased contact surface area, achieving TONs of 11 000 with 50 ppm catalytic loadings at 40 °C under 60 psi ethylene pressure, outperforming G1 catalysts under similar conditions.³⁴ Although turnover numbers (TONs) as high as 1 960 000 have been achieved using Hoveyda–Grubbs analogues bearing spirocyclic alkyl amino carbene ligands, these results typically require elevated ethylene pressures of around 10 bar.³⁵ Experimental and theoretical studies have shown that the rigidity of spirocyclic alkyl amino carbene ligands prevents both bimolecular and β-hydride elimination decomposition of the ruthenium catalyst during ethenolysis reactions, thereby leading to high turnover numbers (TON) and enhanced selectivity.^{35b}

In light of this, we sought to explore the potential of our yolk-shell system to facilitate ethenolysis under atmospheric pressure, aiming to highlight its capacity for ethylene confinement and stabilization within confined reaction spaces. The ethenolysis reactions were carried out in simple Schlenk reactors at atmospheric pressure with catalytic loadings between 0.05–1.00% mol Ru (Scheme 4). The methyl oleate and toluene were degassed before use and the reaction was carried out in pure ethylene gas (99.95%). A Schlenk reactor was charged with MO in toluene (0.05 M) and ethylene gas was bubbled for



Scheme 4 Ethenolysis of methyl oleate.

five minutes throughout the solution at room temperature. After that, the reactor was sealed with a rubber septum and then taken to a pre-heated oil bath and stirred at 40 or 80 °C. Samples withdrawn from the reaction mixture were analyzed by GC-MS. As can be seen in Table 4, the reaction proceeded with high selectivity towards ethenolysis reactions. The major products of ethenolysis reactions are the 1-decene (**2a**) and methyl 9-decenoate (**2b**). The self-metathesis of methyl oleate yields 9-octadecenedioic acid-1,18-dimethyl ester (**3a**) and 9-octadecene (**3b**) (*cis/trans*) as the minor products of the reaction. However, cross or self-metathesis of MO can be suppressed by the presence of excess ethylene. The purity of methyl oleate and the effect of the reaction atmosphere were compared in detail. In the first reaction, the Schlenk reactor was sealed under ethylene atmosphere and a TON value of 1000 was reached after 24 h (Table 4, entry 8). The TON value was decreased to 900 and 640 when the reaction was carried out in nitrogen and air atmosphere.

The catalyst's reusability was tested on RCM of diethyl diallyl malonate in toluene, and the results are given in Table 5. The catalyst showed high performance until the 6th

turn, and its performance was reduced in the 8th run. After the 8th cycle, the catalyst was separated and analysed by ICP-OES, and only 0.5 wt% Ru leaching was observed.

The in-filtrate tests were carried out to determine the catalyst leaching during metathesis reactions (Fig. 7). For this purpose, RCM reactions of diethyl diallyl malonate was carried out using optimum reaction conditions with a catalytic loading of 0.5 mol% Ru (Ru@etch-BTME@SiO₂(1)). At 45% conversion of diethyldiallyl malonate, the reaction mixture was separated into two equal portions. The first portion of the mixture was kept in the Schlenk reactor in contact with the catalyst. The second portion of the mixture was centrifuged and the solution phase was taken to a new Schlenk reactor and magnetically stirred. The first part of the reaction mixture which contains solid catalyst Ru@etch-BTME@SiO₂(1) of the reaction mixture bearing catalyst (in-filtrate) reached complete conversion after 90 minutes. On the other hand, the reaction was nearly stopped in the separated solution phase which is not in contact with the catalysts and the conversion was increased to 46% after 90 minutes of reaction time. These results indicate that the catalyst did not leach during RCM reactions and the RCM reaction proceeds in a heterogeneous manner.

Table 5 Reusability of Ru@etch-BTME@SiO₂ on RCM reactions

Cycle	1	2	3	4	5	6	7	8
Conv. %	99	99	98	97	95	90	72	52
Time (h)	0.5	0.5	0.5	0.5	1	2	4	12

Table 4 Ethenolysis of methyl oleate (99% purity)

Exp.	Ru (mol %)	Time (h.)	Temp. (°C)	Conv. ^a %	Sel. %	TON ^b
1	1	2	40	99	98	100
2	0.5	4	40	99	98	200
3	0.1	8	40	35	98	350
4	0.05	24	40	15	98	300
5	1	0.5	80	99	97	100
6	0.5	1	80	99	99	200
7	0.1	6	80	72	98	720
8	0.05	24	80	50	96	1000
9 ^c	0.05	24	80	45	95	900
10 ^d	0.05	24	80	32	96	640

^a Determined by GC-MS using *n*-tetradecane as internal standard.

^b Turn-over number. ^c N₂ atmosphere. ^d Technical grade methyl oleate (70% purity).

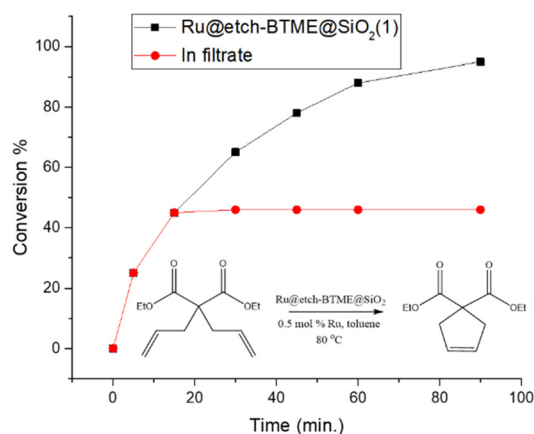


Fig. 7 In-filtrate catalytic test for RCM reactions.

Conclusion

A yolk/void/shell silica support with a hydrophobic shell was used to immobilize quaternary ammonium-tagged Hoveyda-Grubbs catalyst (Aquamet) to obtain a more robust and efficient metathesis catalyst for RCM and ethenolysis reactions. The hydrophobic nature of the yolk-shell material improved the diffusion of hydrophobic substrates within the inner core where the ruthenium catalyst is confined. The catalyst showed high performance in RCM reactions reaching a TON value of 1500 within 8 h of reaction time. The ethenolysis of methyl oleate can be carried out at atmospheric pressure with high selectivity values up to 96%. The catalyst showed moderate reusability and after 8th run, only 2 ppm catalyst lost was observed. The future studies will be focused on direct integration of non-quaternary ammonium group functionalized commercial ruthenium metathesis catalysts and functionalized shell structures for design of smart catalyst systems.

Experimental section

Otherwise noted all chemicals are purchased from Sigma-Aldrich and used as received. Aquamet (4-((4-ethyl-4-methylpiperazin-1-ium-1-yl)methyl)-1,3-dimesitylimidazolidin-2-ylidene)dichloro(2-isopropoxybenzylidene)ruthenium(II) chloride was purchased from Sigma-Aldrich and used without further purification. The catalyst was stored in Schlenk flasks under nitrogen atmosphere at 2–4 °C. Dichloromethane and toluene were dried over P₂O₅ and molecular sieve 4 Å and distilled under nitrogen atmosphere. The solvents were kept under a nitrogen atmosphere in the presence of a molecular sieve 4 Å. Methyl oleate was distilled under vacuum and dried over molecular sieves 4 Å.

Synthesis of nano sized silica gels

Monodisperse silica nanoparticles were synthesized using a modified version of the literature procedures.³⁶ First, ethanol/water mixture (90 mL/10 mL), concentrated ammonia (2.8 mL), non-ionic surfactant; Synperonic®F108 (0.10 g), and cationic surfactant; cetyltrimethylammonium bromide (CTAB, 0.10 g) were added to a 250 mL two-necked glass reactor at room temperature. The solution was stirred mechanically at 180 rpm for 30 minutes. After that, tetraethoxyorthosilane (TEOS, 7.0 g) was added dropwise to the solution and stirred at room temperature for 24 h. After that, the resulting mixture was centrifuged at 5500 rpm for ten minutes to isolate the silica gel particles. The separated silica gels were washed with deionized water and ethanol (20 mL × 2) and dried in oven at 100 °C overnight, followed by calcination at 350 °C for 24 h.

Synthesis of yolk-shell silica with hydrophobic shell (etch-BTME@SiO₂)

A two necked 250 mL glass flask was charged with nano-sized silica gel (1.0 g) and dispersed in 40 mL of deionized water using sonicator for ten minutes and then magnetically stirred

for one hour (mixture A). Another flask (mixture B) was charged with 60 mL of deionized water, 0.30 g of non-ionic surfactant Synperonic®F108 and resorcinol (0.30 g, 2.73 mmol) and the reaction mixture was stirred at room temperature for two hours. After that mixture A and mixture B were mixed in a two necked 250 mL glass flask and after stirring for five minutes at room temperature, 0.3 g cetyltrimethylammonium bromide (CTAB), aqueous NaOH (1.0 M, 700 µL) and 1,2-bis(trimethoxysilyl)ethane (BTME, 340 µL, 1.35 mmol) was added to the reaction mixture and the reaction vessel was taken to a preheated oil bath at 80 °C and stirred for 24 h. After that, the solid particles were separated from the reaction mixture through centrifugation at 6000 rpm for ten minutes. The separated solid particles were then taken to a glass flask and refluxed in ethanol (100 mL) bearing 1 mL of concentrated HCl to remove the surfactants within the yolk-shell particle.

The isolated solid particles were stirred in a concentrated NH₃/acetone (v/v: 1/3; 20 mL NH₃, 60 mL acetone) mixture to form a distinct void space between the core and the shell through etching of the inner core. After 96 h of intense stirring at room temperature, the particles were separated through centrifugation, washed with deionized water (20 mL × 3) and ethanol (20 mL × 2), and dried under high vacuum overnight.

Immobilization of aquamet on etch-BTME@SiO₂

1.0 g of Etch-BTME@SiO₂ and Aquamet (20 mg, 0.0248 mmol) was taken to a Schlenk reactor and the reactor was sealed with a rubber septum. The reactor was then connected to the Schlenk line and degassed under a high vacuum for ten minutes and then nitrogen was purged into the reactor. Dry dichloromethane (15 mL) was then added to the reactor and the reaction mixture was stirred for 4 h at room temperature under nitrogen atmosphere. The solid catalyst particles were separated through centrifugation at 6000 rpm for five minutes and washed with toluene (2 mL × 2) and dichloromethane (1 mL × 1) and dried under high vacuum overnight.

Immobilization of aquamet on nano-SiO₂

Aquamet was immobilized on nano sized silica gel using a similar procedure to that used for etch-BTME@SiO₂. 1.0 g of nano-SiO₂ and Aquamet (20 mg, 0.0248 mmol) was taken to a Schlenk reactor and the reactor was sealed with a rubber septum. The reactor was then connected to the Schlenk line and degassed under a high vacuum for 10 minutes and then nitrogen was purged into the reactor. Dry dichloromethane (10 mL) was then added to the reactor and the reaction mixture was stirred for one hour at room temperature under nitrogen atmosphere. The catalyst was separated through centrifugation at 8000 rpm for ten minutes and washed with toluene (2 mL × 2) and dichloromethane (1 mL × 2) and dried under high vacuum overnight.

Representative procedure for ring-closing metathesis reactions

A Schlenk reactor was charged with Ru@etch-BTME@SiO₂ (5 mg, 0.02356 mmol Ru g⁻¹, 0.18 µmol Ru) in dry toluene (1.2 mL) and stirred for two minutes for the homogenous dis-

tribution of the catalyst. Diethyl diallylmalonate (DEDAM, 0.120 mmol, 30.0 μL) was added to the reactor and the reaction mixture was taken to a preheated oil bath at 80 $^{\circ}\text{C}$. Samples (10 μL) were regularly withdrawn from the reaction mixture, diluted with methanol, and analyzed by GC-MS. The reaction was stopped when the conversion of the substrate reached a plateau.

Representative procedure for ethenolysis of methyl oleate

A Schlenk reactor was charged with Methyl oleate (0.36 mmol, 122 μL) in 2 mL of dry toluene at room temperature and capped with a rubber septum. A stainless-steel needle was dipped into the solution to purge ethylene gas and reactor was connected to a burette to measure the ethylene flow rate and amount. Ethylene gas was bubbled throughout the solution for two minutes (3.0 mL min^{-1}). After that Ru@etch-BTME@SiO₂ (5 mg, 0.02356 mmol Ru g^{-1} , 0.18 μmol Ru) in dry toluene (1.2 mL) was added to the Schlenk reactor and ethylene gas purged from the reaction mixture for an additional two minutes (3.0 mL min^{-1}). The needle was taken out of the reactor and all valves are closed in Schlenk reactor. The reaction mixture was stirred at 80 $^{\circ}\text{C}$ under an ethylene atmosphere. Samples were regularly withdrawn from the reaction mixture and analyzed by GC-MS. Once the conversion of methyl oleate has reached a plateau.

Reusability of the catalyst in RCM reactions

A Schlenk reactor was charged with Ru@etch-BTME@SiO₂ (20 mg, 0.02356 mmol Ru g^{-1} , 0.72 μmol Ru) in dry toluene (4.8 mL) and stirred for two minutes for the homogenous distribution of the catalyst. Diethyl diallylmalonate (DEDAM, 0.480 mmol, 120.0 μL) was added to the reactor and the reaction mixture was taken to a preheated oil bath at 80 $^{\circ}\text{C}$. Samples (10 μL) were regularly withdrawn from the reaction mixture, diluted with methanol, and analyzed by GC-MS. The reaction was stopped when the conversion of the substrate reached a plateau. The reaction mixture was centrifuged to separate the catalyst from the reaction mixture. The separated solid catalyst particles were washed with toluene (1 mL) and then taken to a fresh reactor-bearing diethyldiallyl malonate in toluene and used in the next catalytic cycle. At the last cycle, the solid particles were separated again and washed with toluene and dried under vacuum overnight and then ruthenium content was analyzed by ICP-OES and after 8th cycle only a ruthenium leaching of 0.2 wt% was observed.

Data availability

Additional high contrast TEM and SEM images for the core/shell particles, as well as XPS spectrum of materials were given in ESI[†] section. The data supporting this article have been included as part of the ESI[†].

Conflicts of interest

There are no conflicts to declare.

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