Solid Supported Ruthenium Complexes for Olefin Metathesis

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Abstract: Immobilization of ruthenium metathesis catalysts on solid supports has attracted much attention in recent years since it opens up the possibility for easy catalyst-product separation and catalyst reuse as well as reduction of the residual ruthenium content in the organic product. The state of the art on immobilization of ruthenium based metathesis initiators on solid supports is surveyed in this review. In addition, a comparison of the performance of the heterogenized catalysts with homogeneous analogues is made.

Keywords: Alkylidene, Immobilization, Inorganic supports, Heterogeneous catalysis, Olefin Metathesis, polymeric supports, ruthenium carbene, ruthenium.

1. INTRODUCTION

The development of easy to handle, well-defined ruthenium-based alkylidene complex 1 [1] which combine remarkable tolerance towards functional groups and moisture with high activity has tremendously broadened the scope of metathesis reactions as a powerful synthetic tool [2]. The optimization of the activity of the catalysts for various applications in metathesis reactions normally proceeds by tuning the ligand sphere around the corresponding metal center. Thus replacement of a phosphine by a highly electron donating N-Heterocyclic carbene (NHC) has afforded catalyst 2 with increased reactivity by many orders (Fig. 1) [3].

![Fig. (1). Ruthenium alkylidene metathesis initiators.](image)

Similarly, the introduction of the bidentate alkylidene by Hoveyda resulted in metathesis catalysts 3 and 4 with increased stability and excellent recyclability (Fig. 1) [4]. On the other hand, the advance of the 1\textsuperscript{st} and 2\textsuperscript{nd} generation ruthenium indenylidene 5 [5] and 6 [6] proved to have higher thermal stability than their benzylidene counter parts. Additionally, Verpoort et al. reported ruthenium indenylidene Schiff base complexes 7 and 8 as stable and effective metathesis initiators (Fig. 2) [7].

However, in spite of the highly favorable properties of the homogeneous well-defined ruthenium metathesis initiators, they are difficult to separate from the reaction mixture and often impose significant challenges. Very recently, different strategies for the sequestration of ruthenium impurities from olefin metathesis postreaction mixtures have been reviewed by G. C. Vougioukalakis [8]. Nonetheless, the residual ruthenium complex may cause problems such as olefin isomerization, decomposition of the product, and increased toxicity of the final materials. Therefore, immobilization on various supporting materials combines the advantages of conventional heterogeneous catalysts with the versatility of homogeneous ones as heterogeneous catalysts not only allow for easiness of separation and recovery from the reaction medium but also show repeated recycling potential, good stability and ease of handling.

Up to now, different soluble polymers and solid supports are used as carriers to recover catalysts. Furthermore, various solvent systems such as perfluorinated solvents, ionic liquids, and supercritical CO\textsubscript{2} are also employed for this purpose. The present review describes the current state of the art on immobilization of ruthenium based metathesis initiators on solid supports. The immobilisation of the catalysts on polymeric beads, monolithic materials and siliceous supports both mesoporous as well as temploral will be discussed. In addition, the performance of the supported catalysts will be compared with the homogeneous analogues.
Grubbs and coworkers described the first example of a polymer supported well-defined olefin metathesis catalysts [11]. They reported a series of olefin metathesis catalysts based on a ruthenium vinyl carbene complex attached on a 2% cross-linked polystyrene divinyl benzene solid support (DVB-PS) (Scheme 1). The ability of vinyl carbene complexes to exchange its phosphine ligands with a variety of phosphines allowed the convenient synthesis of PS-DVB supported ruthenium bis-phosphine vinyl carbene catalysts 9-11. However, the supported catalysts turned out to be less appropriate for polymerization relative to their homogeneous counterparts, which was attributed to phosphine chelation effects, diffusion limitations and incomplete substitution of phosphine. The general decrease in metathesis activity of these PS-DVB-supported catalysts is offset by the extended lifetime of the supported catalysts. The PS-DVB-supported ruthenium catalysts are long-lived and can be re-used in practical circumstances.

Blechert et al. [12] reported for the first time Merrifield polystyrene (1% divinyl benzene) (DVB) bound catalyst 12 anchored by a NHC ligand. They anticipated that anchorage of the catalyst through the NHC ligand could result into permanently immobilized and highly active metathesis initiator since NHC ligands remain bonded to the ruthenium center during metathesis reactions. The supported catalyst 12 was synthesized with a loading level between 0.14 and 0.4 mmol.g⁻¹ of Grubbs’ catalyst 2 by ligand exchange with the polymer supported 3,4-dimethyl-4-dihydroimidazoline chloride (Scheme 2). The catalyst was tested on its ring-closing metathesis (RCM) activity towards various substrates and showed

2. POLYMER BEADS SUPPORTED RUTHENIUM METATHESIS CATALYSTS

Functionalised polystyrenes present as linear or cross-linked polymers are very often used as catalyst support [9]. They are available in different bead sizes (50-500 mm) and degrees of functionalisation and cross-linking [10].
full cyclization. However, the rate of cyclization is lower relative compared to the homogeneous analogues. Highly pure products were obtained after filtration as the only purification step. The ease of isolation allows automation and makes catalyst 12 particularly suitable for combinatorial applications.

In addition, the same group also reported on the heterogeneous Hoveyda type ruthenium catalyst 13, obtained by immobilization on a Merrifield resin via a styrene ligand [13]. The supported catalyst 13 is an excellent initiator in olefin metathesis reactions, re-usable and tolerates a wide variety of functional groups. Krischning and coworkers applied a similar approach however the linkage to the polymer is of ionic character [14].

A ruthenium alkylidene metathesis catalyst has been supported on a vinyl polysyrene polymer by means of metathesis between Grubbs’ catalyst 1 and vinyl polysyrene to afford heterogeneous catalyst 14 [15]. Nevertheless, the immobilized catalyst was found to be unstable and degrades over a period of about 5 hours and if then isolated by filtration from the resin, found to be inactive. It has been suggested that the decomposition is due to the ring-closing metathesis between ruthenium alkylidene and free vinyl groups present in the resin releasing the unstable ruthenium methyliden 15 in solution (Scheme 3). This immobilized catalyst has been used to initiate ring-opening metathesis polymerization (ROMP) of norbornene derivatives onto a polymer support to prepare novel high-loading resins for use in combinatorial chemistry.

Procopiou reported vinyl polysyrene polymer supported ruthenium pro-catalysts 16 and 17 that becomes homogeneous in the course of ring closing metathesis (RCM), with concomitant reaction rate advantages, and then recaptured by the resin after completion of the reaction in solution, a ‘boomerang’ catalysts (Scheme 4). In the preparation of the 1st generation boomerang catalyst 16 preparation time was found to be critical, longer catalyst-resin preparation times (>2 h) tended to lead to poorly active catalyst for RCM [16].

Compound 16 was found to be an effective catalyst for ring closing metathesis. The reaction rate and activity was found to be comparable to the homogeneous Grubbs' catalyst 1. In addition, the catalyst could be recycled and re-used up to three times by simple filtration. However, deterioration of the catalyst activity was noticed and could be reduced by addition of volatile hexane. The ruthenium residues in the product mixtures were much lower compared with the reported values using catalyst 1 and comparable to the procedure reported by Grubbs applying phosphine [17]. In contrast to 16, the second-generation boomerang catalyst 17 still retained activity in RCM after three consecutive runs [18] (Scheme 4).

Nolan’s group reported additional boomerang catalysts [19], they used macroporous pol-DVB to prepare heterogeneous ruthenium catalysts 18-22 (Scheme 5). Macroporous poly-DVB has advantages over lightly cross-linked Merrifield resins in that the permanent well-developed porous structure in macroporous resins can be easily accessed by solvents and reactants without any need for swelling [20]. In ring-closing metathesis the immobilized catalysts show comparable or better reactivities than their homogeneous counterparts, they perform very well with dienes and moderately well with highly hindered substrates. The macroporous poly-DVB supported catalysts tolerate functional groups very well and in some cases they are recyclable.

Scheme 7. Hydrophilic polymer supported ruthenium alkylidene metathesis initiators.

TentaGel resin due the presence of amino functionalized dimethyl acrylamide and mono-2-acrylamidopropyl polyethylene glycol, and proved to be perfectly stable under metathesis conditions.

A new amphiphilic, polymer-bound variant of the Hoveyda-Grubbs catalyst was synthesized (28) via the coupling reaction of a carboxylic acid-functionalized poly(2-oxazoline) block copolymer with 2-isopropoxy-5-hydroxystyrene and subsequent reaction of the resulting macroligand (Fig. 4) with Grubbs' catalyst 2 [25]. A turnover number (TON) of up to 390 was achieved for the ring-closing metathesis of diethyl diallyl malonate in water resulting in the first high value for an aqueous RCM reaction. For the first time, recycling of a ruthenium initiator in an aqueous RCM reaction has been successful to some extent. In addition, the micellar conditions accelerate the conversion of the hydrophobic diene and at the same time stabilize the active alkylidene species, although competing decomposition of the catalyst in water still impairs the catalyst performance. The residual ruthenium content was determined to be below 1ppm in the product suggesting a very low leaching of the polymeric catalyst system.

Fig. (3). PEGA-NH₂ resin.

Fig. (4). Carboxylic acid-functionalized block copolymer.

A series of ruthenium carbene complexes were permanently immobilized on polymer supports using carboxylate ligands as linking groups. For this objective one or both chloride ligands from parent ruthenium complexes were replaced with an immobilized carboxylic acid. For instance, polystyrene (PS) resin supported catalyst 29 was afforded as a new heterogeneous catalyst with a ruthenium loading of about 0.035 mmol g⁻¹ by replacing one chloride ligand from complex I [26] (Scheme 8). The supported catalyst is highly active in self-metathesis of internal alkenes and performed
even better than Grubbs’ catalyst 1. In the RCM of diethyl diallylmalonate, applying catalyst 29, better results were accomplished compared with for example catalyst 23 reported by Dowden and Savovic [21]. Catalyst 29 was easily separated from the metathesis products and reused without the addition of any stabilizing agents, although some leaching and deterioration of the catalyst was observed.

The Grubbs-Hoveyda type metathesis catalysts have also been immobilized on a perfluoroglutaric acid derivatized polystyrene-divinylbenzene (PS-DVB) by chlorine exchange [27]. While the substitution of one chloride ligand of the parent Grubbs-Hoveyda catalyst afforded catalyst 30 the substitution of both chloride ligands by addition of CF$_3$COOAg to 30 led to catalyst 31. In RCM of representative substrates both catalysts possess high activities, catalyst 31 being the superior system with TONs up to 1100 while with catalyst 30 TONs of 380 were achieved. For both systems, 30 and 31, the leaching of ruthenium into the reaction mixture was unprecedentedly low, resulting in a ruthenium content < 70 ppb in the final RCM-derived products.

Furthermore catalysts 32 and 33 were synthesized by reaction of Grubbs catalyst 2 and Grubbs-Hoveyda catalyst 3 respectively with a perfluoroglutaric acid derivatized polystyrene-divinylbenzene (PS-DVB) support [28]. Supported catalysts were prepared with high loadings (2.4 and 22.1 mg of catalyst/g PS-DVB for 32 and 33 respectively). Catalysts 32 and 33 represent the first permanently bound versions of both Grubbs’ catalyst 2 and the Grubbs-Hoveyda catalyst 3. Catalyst 32 exhibited a higher activity while catalysts 31 and 33 displayed significantly reduced activities in RCM compared to their homogeneous analogues. Hence, with 32, turnover numbers (TONs) up to 4200 were realized in stirred-batch (carousel) RCM experiments. Leaching of ruthenium into the reaction mixture was low, resulting in ruthenium contents of 70, 83 and 15 ppb, respectively for catalysts 31, 32 and 33.

Polymer supported ruthenium catalyst 34 was prepared via vacuum-driven anionic ligand exchange of a polymer supported perfluorocarboxylic acid with ruthenium-bound perfluorocarboxylates in mesitylene [29] (Scheme 9). The polymer-supported catalyst 34 is active for RCM of DEDAM and can be recycled. However, the activity is considerably reduced compared to its homogenous counterpart.
3. MONOLITH SUPPORTED RUTHENIUM METATHESIS INITIATORS

In order to overcome the problems commonly related to heterogeneous systems, such as diffusion controlled reactions and catalyst bleedings among others, Buchmeiser was able to immobilize Grubbs' type ruthenium initiators on non-porous, ring opening metathesis polymerization derived monolithic materials generated by well-defined transition metal alkylidenes. This polymerization method allows for the synthesis of monolithic materials with controlled and highly reproducible porosity characteristics. In addition, it allows for the development of monolithic supports with diversity of functional groups [30].

Using Grubbs' catalyst 1 ROMP initiator, they managed to synthesize a number of functionalized monolith supports suitable for catalysts immobilization. For instance, a N-heterocyclic carbene precursor was successfully grafted onto the surface of monolithic materials [31]. The immobilized catalyst 35 (Scheme 10) with a loading of up to 1.4 mg g⁻¹ was achieved from immobilized NHC following the standard procedure. The catalyst possesses a high activity towards RCM as well as towards ROMP. The cis/trans ratio of the polymers is exactly the same as the one obtained in homogeneous polymerizations (90 % trans).

The prepared monolithic systems may be used either as pressure-stable reactors or (in miniaturized form) as cartridges for applications in combinatorial chemistry. Additionally, the use of NHC ligands even in RCM successfully suppresses any bleeding of the column, consequently allowing the synthesis of virtually ruthenium-free cyclization products with a ruthenium content ≤ 70 ppm.

Different versions of monolith supported metathesis catalysts were obtained by chloride exchange between Grubbs' catalyst 2 and monolith supported silver carboxylates [32] (Scheme 11). Heterogeneous catalysts 36, 37 and 38 with loading of 10, 7 and 9 mg g⁻¹ respectively were realized using this protocol. The catalysts were used in ring-closing metathesis of various substrates allowing turnover numbers (TON's) close to 1000. In a flow-through set-up, an auxiliary effect of pendant silver carboxylates was observed with catalyst 38, where the silver moiety functions as a (reversible) phosphine scavenger that both accelerates initiation and stabilizes the catalyst by preventing phosphine elution. In all RCM experiments ruthenium leaching was low, resulting in a ruthenium content of the RCM products ≤ 3.5 µg g⁻¹ (3.5 ppm).

The Grubbs-Hoveyda catalyst 4 has been immobilized on a monolithic support by exchanging chloride ligands between the ruthenium initiator and a monolith supported fluorinated carboxylate [33]. For this purpose norborn-2-ene-based perfluorinated acid was grafted onto the surface of the monolith before being deproto- nated and converted into the corresponding silver salt. Reaction of the thus modified support with complex 4 resulted in the formation of a mono-carboxylate substituted complex. Finally, the remaining chloride ligands were reacted with CF₃COOAg to yield the corresponding bis-carboxylate substituted catalyst 39 (Scheme 12). In this manner a ruthenium loading of the monolith-supported catalyst 39 of 0.41 mg g⁻¹ was obtained.

Scheme 10. Monolithic supported metathesis catalyst 35.

Scheme 11. Monolith-supported catalysts obtained via chloride exchange.

Scheme 12. Monolith supported Grubbs-Hoveyda type catalyst.
Scheme 13. Disc-shaped monolith-supported catalysts 40 and 41.

Most importantly, only pure product as well as unreacted ad-
duct could be found in the eluent, which directly translates into an
increased long-term stability of the catalysts. Extremely low leach-
ing (<0.2%) was observed resulting in product contamination with
ruthenium and silver of 1.8 and 0.01 ppm, respectively.

Buchmeiser and co-workers extended the study by focusing on
disc-shaped monoliths to immobilize ruthenium initiators in con-
trast to previously reported one. The disc-shaped monoliths were
developed by cutting the parent monolith into pieces of 1 cm in
height and subsequently used in the preparation of catalysts 40 and
41 (Scheme 13).

The supported catalyst 40 was prepared with loadings of about
2.5 wt% [34]. Excellent reactivities were observed in RCM and
ROCM of various substrates. The monolithic disk immobilized
catalyst 40 showed somewhat reduced activity, yet compared to the
homogenous analogue, still can be regarded as good. In terms of
product purity, it is noteworthy that ruthenium leaching from the
supported systems 40 was very low, resulting in ruthenium con-
taminations of less than 0.14 ppm.

With the disc shaped monolith supported catalyst 41 [35] on the
other hand, TONs in the range of 60-330 were obtained in the ring-
closing metathesis of representative substrates which are compara-
table to those obtained with the homogenous analogue.

These relatively low activities clearly stems from the fact that
reactions within the disks were not stirred and, therefore, depended
on diffusion of the substrates to the catalytic site. Nevertheless, the
reactivity observed with these systems definitely justifies the use of
such monolith-supported catalysts in high-throughput screening,
where the disk serves simultaneously as support, reaction vessel,
and filtration unit and can, in principle, be directly used in combina-
tion with commercially available machines.

Hoveyda and co-workers [36] disclosed the one-pot synthesis of
ruthenium complexes 42-44 supported on commercially available
monolithic samples of porous sol-gel glass (Scheme 14). The sup-
ported catalysts can effectively promote various olefin metathesis
reactions and can be easily employed in a library synthesis format
without multiple weighing, in air and with undistilled commercial
reagent-grade solvents. Catalyst recovery is simply carried out with
a pair of tweezers; it does not require filtration and generates mini-
mal solvent waste. The catalyst retains its activity after multiple
Silica-gel immobilized Hoveyda–Grubbs type catalysts 45a and 45b synthesized by alkylidene exchange between commercially available Grubbs' catalysts (1 and 2) and silica gel immobilized isopropanoxystyrene has been reported by Blechert et al. [37] (Scheme 15). The supported catalysts showed good stability on storing at 4 °C under nitrogen over two weeks without any sign of decomposition. However, when quantitative loading of the styrene with ruthenium was achieved the catalysts decomposed within days at -20 °C. The catalysts demonstrate higher activity in a number of metathesis test reactions than the parent Grubbs' catalysts and they can be easily separated by simple filtration of the non-swelling material.

The hybrid organic-inorganic silicas obtained as bridged silsesquioxanes from a bis-silylated Hoveyda-type monomer via the sol-gel process have been prepared for the first time by Moreau [38]. Important to note is that the sol-gel process allows the control of not only the loading of organic groups but also their distribution in the matrix in contrast with grafting approach. Three different types of hybrid materials were prepared from bis-silylated compound 46 (Scheme 16). Co-gelification with tetraethoxysilane (TEOS) afforded 47a, whereas hydrolytic polycondensation of monomer 46 without TEOS in the same nucleophilic conditions gave 47b. Another sol-gel condition was tested with neat monomer 46 in order to get an organized and porous material, using dodecylamine both as basic catalyst and surfactant, and gave rise to material 47e. Capping of the residual silanol groups was performed before changing with the metal in order to test if improved materials could be obtained, as the silylated hybrid is less hygroscopic than its parent one and gave rise to 47aSi. All materials (47a-e and 47aSi) were charged with the metal by treating them with the Grubbs' catalyst 2. The cata-

\begin{align*}
45a & : L = H_2\text{Mes} \\
45b & : L = PCy_3
\end{align*}

Scheme 15. Immobilized Hoveyda–Grubbs' type catalysts on silica gel.

cycles (>15), affording products that are of high purity without resorting to any purification steps.

4. NON POROUS SILICA SUPPORTED RUTHENIUM METATHESIS INITIATORS

Inorganic silica material is a common support for the heterogeneousization of molecular catalysts. It offers a considerable advantage over other supporting materials due to its excellent thermal and chemical stability, low cost, and broad solvent compatibility. It has a rigid structure, does not swell in solvents, and can be used at both high and low temperatures and pressure.

\begin{align*}
si\text{(OE)3} & \quad si\text{(OE)3} \\
46 & \quad 46
\end{align*}

\begin{align*}
a) & \text{40 TEOS, H}_2\text{O,} \\
b) & \text{H}_2\text{O,} \\
c) & \text{C}_6\text{H}_{12}\text{NH}_2, \text{H}_2\text{O,EtOH}
\end{align*}

47

\begin{align*}
47a & \\
47aSi
\end{align*}

\begin{align*}
47a & \quad x = 40, \text{ condition a} \\
47b & \quad x = 0, \text{ condition b} \\
47c & \quad x = 40, \text{ condition c}
\end{align*}

\begin{align*}
47 & \quad x = 40, \text{ condition c}
\end{align*}

Scheme 16. Preparation of ruthenium heterogeneous catalysts 48a-c and 48aSi.
Silica gel supported catalysts 49 and 50.

Scheme 17. Silica gel supported catalysts 49 and 50.

Catalysts proved their efficiency as recyclable catalysts in the ring-closing metathesis of dienes and enynes. The materials prepared from the sol-gel are superior to the same catalysts deriving from anchorage to meso-structured silica. Furthermore, end capping of residual silanol groups before charging with the metal does not improve the materials.

The second-generation Grubbs catalyst type has been successful immobilized on both porous and non-porous silica via the NHC ligand [39]. For this purpose the porous and nonporous silica were functionalized with a NHC-precursor and subsequently converted to heterogeneous 49 and 50 applying the standard procedure (Scheme 17). Ruthenium loadings of 5.3 and 1.3 mol.% were realized. Additionally, coating techniques were applied, where C18-derivatized silica-60 was used to attain a heterogeneous catalyst with a 4.1 mol.% ruthenium loading.

In RCM of DEDAM, the catalyst immobilized onto non-porous silica reached the maximum turnover number (TON) of 75. Interestingly, basically identical results (TON ≈ 80) were obtained with catalysts immobilized onto porous silica. Nevertheless, the low TON’s (51) obtained with other less reactive compounds such as 1,7-octadiene, N,N-dialkyl trifluoracetamide, dialkyl ether, and dialkyl diphenylsiline suggest that the stirred batch setup with this type of support is highly diffusion controlled, where reaction is too slow and decomposition of the intermediary ruthenium methyldiene dominates.

Catalytic results obtained with coated supports exceed the data for TON of all other silica supports by far. This can be interpreted in a way that a support containing only macropores facilitates diffusion. It is worth mentioning that in all cases a quantitative retention of the original amount of ruthenium at the support was revealed thus offering access to metal-free products.

A ruthenium-carbene complex 51 bearing a hydroxalkyl group on the N-substituent of its NHC ligand reported by the Fürstner group [39] has been covalently immobilized on chloro-functionalized silica (Scheme 18). Although a longer reaction time is necessary to reach complete conversion, the immobilized catalysts 52a-b possess a RCM performance comparable to its homogeneous analogues. These catalysts 52a-b offer the advantage to be reusable up to three times. However, in case the immobilization of the hydroxalkyl-functionalized ruthenium carbene complex is done by physisorption rather than chemisorption, rearrangement of 51 to isomer 53 was observed bearing the neutral ligands in a cis rather than the usual trans position (Scheme 19), which is a characteristic of the highly conserved structural feature of the Grubbs type ruthenium carbene complexes.

The silica-supported catalysts 54 and 55 have been successfully prepared via triethoxysilyl-functionalized NHC ligands [40] (Scheme 20). These species were shown to be competent catalysts for a variety of olefin metathesis reactions, mimicking their homogeneous counterparts. Likewise, the activity of the supported cata-

Scheme 18. Immobilization of complex 51 by chemisorption.

Scheme 19. Immobilization of complex 51 by physisorption.
that the catalysts do not leach ruthenium under the standard reaction conditions as ruthenium concentration of the filtrate of less than 5 ppb in all cases are obtained.

Buchmeiser et al. [41] reported catalysts 56 and 57 developed by exchange of chloride from Grubbs' catalyst 2 with immobilized silver carboxylates (Scheme 21). Interesting to mention is that only one chloride ligand was exchanged. Catalyst loadings of 42 and 63 mg g⁻¹ respectively were achieved. These heterogeneous catalysts are competent catalysts in ring-closing metathesis of various substrates allowing turnover numbers (TONs) close to 1000. In all RCM experiments ruthenium leaching was low, resulting in a ruthenium content in the RCM products ≤ 3.5 g g⁻¹ (3.5 ppm).

One or both chlorides in the Hoveyda-Grubbs type catalysts have also been selectively substituted in the preparation of heterogeneous catalysts containing mixed anionic ligands as well as disubstituted catalysts. After heterogenization of the catalysts, the remaining free SiOH groups on the silica surface were subsequently capped with dimethyldimethyldisiloxane.

Loadings between 31 and 65 μmol g⁻¹ were achieved for catalysts 58-63 [42] (Scheme 22). These heterogeneous catalysts showed good stability when stored at +4 °C under argon for 4 weeks without any sign of decomposition. The silica gel bound catalysts containing mixed anionic ligands 58 and 59 were more active in RCM reaction with N,N-diallyl-4-methylbenzenesulfonylamide than their disubstituted counterparts 60 and 61, however, there was not such a marked difference. The supported catalysts 58-
Scheme 23. Immobilized ruthenium complex 64.

Scheme 24. G1-dendrimer ruthenium initiator 65 and its star polymer.

65 displayed considerable lower TONs than their homogeneous counterparts. Nonetheless, compared to similar polymer-bound systems reported by Buchmeiser et al. the prepared silica bound catalysts performed better.

On the other hand, heterogeneous metathesis catalyst 64 was prepared with a ruthenium loading of about 0.78 wt % [43] (Scheme 23). The catalyst demonstrated its activity and high selectivity in ring closing metathesis of 1,7-octadiene and diethyl diallylmalonate, as well as in the ring opening metathesis polymerization of norbornene and cyclo-octene, both carried out in a batch stirred reactor. Almost negligible leaching of ruthenium was observed and successful catalyst reusing was achieved. However, the reaction rate was lower in comparison with its SBA-15 supported analogue.

Synthesis of a new metathesis initiator 65 by coupling ruthenium-complexes to low generation carbosilane dendrimers, 0th generation (G0–Ru) and first generation (G1–Ru) has been reported by Verpoort et al. [44] (Scheme 24). The attachment of the ruthenium complexes to the boundary of the dendrimer is performed by olefin metathesis. With a dendrimeric support the regular occupation of the surface and the good accessibility of all the active catalytic sites for the reactants favors a high activity and selectivity. Besides, product separation is possible via ultra filtration. This dendrimer supported initiator shows a very high activity for the ROMP of norbornene. By using this dendrimeric initiator multi-arm star polymers can be developed in a controlled manner.

The Hoveyda-Grubbs catalyst 4 was successfully immobilized on commercial silica in pellet and powder form following a practical and fast synthesis procedure [45]. A solution of 2nd generation Hoveyda-Grubbs catalyst was brought in contact with a suspension of silica and stirred at 293 K for two hours. A bright greenish powder was acquired with a ruthenium loading of about 0.1 wt %.

The activity of the solid system is truly efficient in various metathesis reactions and stable for at least 4000 TONs. Ruthenium contamination of the products was very low (ppb level). The catalyst can be recycled up to four cycles with full conversion in each cycle. The successful use of the robust system has even been demonstrated in a continuous reactor set-up.

5. MESOPOROUS MOLECULAR SIEVES SUPPORTED RUTHENIUM METATHESIS INITIATORS

In 1992, the preparation of MCM-41 denotes a groundbreaking development in hybrid catalysis [46]. The creation of a uniform mesoporous skeleton delivers a new mean of immobilization. The large pore size allows large organic and organometallic molecules to pass through the channels and provides optimal contact with the surface. In addition, the regular pore size of MCM-41 can provide shape selectivity not provided by classical inorganic supports. This feature has led to a continuous increase in a number of reports about immobilization of ruthenium metathesis initiators on mesoporous materials.

For instance, heterogeneous catalysts 66 and 67 have been prepared by phospine exchange between Grubbs' type ruthenium-alkylidene complexes and a phosphinated mesoporous matrix (P-MCM-41) [47] (Scheme 25). The exchange of a phospine ligand of the homogeneous complex by a P-functionalized spacer molecule was favored due to the increased pKa or donor capacity of the immobilized phosphine ligand. Both catalysts 66 and 67 reveal activity in ROMP of norbornene, however, due to diffusion limitations an enhancement in polydispersity was exhibited for the ROMP of norbornene catalyzed by 66. Noteworthy is that catalyst 67 even exposes metathesis activity in aquatic environment. The RCM activity of catalysts 66 and 67 is in agreement with that of their homogeneous analogues.

Scheme 25. MCM-41 supported Grubbs' type metathesis catalysts.

Ligand exchange between phosphinated mesoporous silica (SBA-15) and either complex 2 or complex 68 has resulted into catalysts 69 with ruthenium attached to the surface via a PCy3-
linker. On the other hand, catalyst 70 with ruthenium attached via a pyridine ligand has been prepared by ligand exchange between pyridinated mesoporous silica and either complex 2 or complex 68 [48]. Both complexes 2 and 68 generated catalysts with the same structure, however, the usage of complex 68 is preferable since catalysts with high loadings are more easily achieved (Scheme 26).

Hybrid catalysts with ruthenium attached to the surface via PCy2-linkers exhibited a higher activity and stability in metathesis than those having ruthenium attached via pyridine linkers. The former catalysts displayed a high activity in a series of metathesis reactions (RCM, ROMP and CM), reaching turnover numbers from 200 to 2000 at nearly 100 % selectivity and being reusable for several times. Catalysts with pyridine linkers tended to decompose rapidly at incomplete conversions. The filtration tests for all catalysts suggested that the immobilized catalysts were responsible for the catalytic activity during the reactions. Ruthenium leaching in the final reaction mixture was very low for catalysts coordinated to PCy2-linkers and even negligible for catalyst with pyridine-linkers.

Shi and coworkers reported catalyst 71, where the ruthenium catalyst is covalently anchored inside the pore channels of SBA-15 via an NHC-ligand [49] (Scheme 27). The outer surface of SBA-15 was masked with Si-CH3 groups before being functionalized with the ruthenium complex guaranteeing that the immobilization took place inside the pore and not outside. This approach was made in order to avoid the decomposition of the catalyst.

The heterogeneous catalyst 71 displays activities in RCM of DEDAM comparable with its homogeneous analogue proving that the reaction, most probably, is not diffusion-controlled due to the three-dimensional channels and high porosity of SBA-15. The immobilized catalyst can be repeatedly used without any apparent decrease in catalytic activity along with the cycle times.

MCM-41 supported Grubbs-Hoveyda type ruthenium complexes 72 and 73 have been reported by Moreau. These heterogeneous catalysts were realized by anchoring a bis-silylated monomer on meso-structured silica MCM-41 followed by the metatation
Mesocellular foam (MCF) supported Hoveyda-Grubbs catalysts have been successfully developed by Yinga et al. [51]. The ultra large pores and high surface area of MCF allowed the ligands and catalytic complexes to be immobilized without steric hindrance, and facilitated the diffusion of bulky substrates during reaction. The resulting novel heterogeneous catalysts 74a and 74b demonstrated excellent activity and reusability for the RCM of various types of substrates (Scheme 29). Although the gradual loss of activity was unavoidable in multiple recycling runs, introducing additional MCF-supported free ligand significantly enhanced the reusability of the heterogeneous catalyst.

Scheme 29. MCF immobilized catalyst 74.

A siliceous mesocellular foam (MCF) immobilized ruthenium metathesis catalyst 75 was efficiently achieved by using click chemistry for linkage with the support [52] (Scheme 30). A ruthenium loading of 0.16 mmol·g⁻¹ was obtained for catalyst 75, while the ligand density of immobilized ligand was 0.19 mmol·g⁻¹ implying that more than 80% of the immobilized ligand was loaded with ruthenium. The supported catalyst 75 is applicable to a designed reactor system that made use of immobilized catalysts in a continuous process by just circulating the reaction mixture to facilitate the removal of in situ generated by-products [53]. The catalyst exhibited good activity and recyclability in RCM of various substrates. In most cases, good catalytic activities were maintained for 5 to 10 runs at 50 °C in DCM.

Scheme 30. MCF immobilized catalyst 75.

Heterogeneous metathesis catalysts 76a and 76b were prepared by immobilization of commercially available Hoveyda-Grubbs type catalyst on siliceous mesoporous molecular sieves SBA-15 via exchange of chloro-ligands by silver(I) carboxylate [43] (Scheme 31). The catalysts proved their activity and high selectivity in ring closing metathesis of 1,7-octadiene and DEDAM, as well as in the ring opening metathesis polymerization of norborne and cyclooctene, both carried out in batch stirred reactor. Almost negligible
leaching of ruthenium was observed and successful catalyst reusing was achieved. However, the reaction rate was slower in comparison with the parent Hoveyda-Grubbs alkylidene under the same reaction conditions. In ROMP, high molecular weight poly(NBE) and poly(COE) were prepared in good or moderate yields.

Importantly, work-up of the RCM reaction simply consisted of the removal of the catalyst through filtration and evaporation of the solvent under vacuum. It is noteworthy that both strained and low strained cyclo-olefins (e.g. norbornene or norbornene derivatives and cyclo-octene) displayed a high reactivity in RCM by using both catalytic systems 77 and 78, under normal reaction conditions. Interestingly, in ROMP, catalyst 77 proved to be more active than catalyst 78. This result is in sharp contrast to the results obtained from RCM reactions using the same catalytic systems.

Zhan catalyst 79 developed by Zannan (Fig. 5) was immobilized on mesoporous molecular sieves MCM-41 and SBA-15 by mixing a suspension of 79 and mesoporous sieves in toluene at room temperature [55]. The immobilization proceeded quickly in a nearly quantitative way. Heterogeneous catalysts prepared in this way exhibited a high activity and 100% selectivity in the RCM of various substrates, and in the ROMP of cyclo-octene. Ruthenium leaching was found to depend on the polarity of the used substrates and solvents. For instance, the lowest leaching (0.04% of the catalyst ruthenium content) was found for the RCM of 1,7-octadiene in cyclohexane. On the other hand, for the RCM of DEDAM in dichloromethane, leaching reached up to 14% of the initial ruthenium content. Results from UV-Vis and XPS studies suggested that catalyst 79 was attached to the mesoporous sieve surface by non-covalent interactions. Approximately 76% of the ruthenium content could be recovered from the sieve at 79 by washing heterogeneous 79 with THF at room temperature.

6. SUPPORTED RUTHENIUM METATHESIS INITIATORS ON OTHER SOLID SUPPORTS

Bannwarth presented for the first time, RCM reactions employing covalently immobilized Hoveyda-type catalysts in scCO₂ as the sole reaction medium [56]. He designed a new hybrid support material with a rigid core structure covered by an ultra-thin layer (~10 nm) of an acrylicamide-styrene copolymer (Fig. 6). The new support
of the supported catalysts found to be dependent on parent homogeneous catalysts, the nature of the support materials as well as immobilization techniques employed. The obtained information concerning the different supported catalysts might be helpful in the design of further immobilized catalysts.

**CONFLICT OF INTEREST**

The authors confirm that this article content has no conflicts of interest.

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**REFERENCES**


