

Review

SBA-15 as a Support for Effective Olefin Metathesis Catalysts

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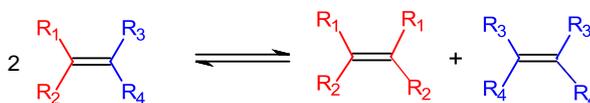


Abstract: Olefin metathesis is the catalytic transformation of olefinic substrates, finding a wide range of applications in organic synthesis. The mesoporous molecular sieve Santa Barbara Amorphous (SBA-15) has proven to be an excellent support for metathesis catalysts thanks to its regular mesoporous structure, high BET area, and large pore volume. A survey of catalysts consisting of (i) molybdenum and tungsten oxides on SBA-15, and (ii) molybdenum and ruthenium organometallic complexes (Schrock and Grubbs-type carbenes) on SBA-15 is provided together with their characterization and catalytic performance in various metathesis reactions. The comparison with catalysts based on other supports demonstrates the high quality of the mesoporous molecular sieve SBA-15 as an advanced catalyst support.

Keywords: olefin metathesis; SBA-15; mesoporous molecular sieve; Mo and Ru hybrid catalysts

1. Introduction: Olefin Metathesis and the Basic Properties of Santa Barbara Amorphous (SBA-15)

Olefin metathesis is the catalytic transformation of olefinic substrates. In this process, C=C double bond splitting is followed by the combination of alkylidene molecular fragments. This general reaction involves aliphatic alkenes, cycloalkenes, dienes, and polyenes, with or without functional groups (Scheme 1).

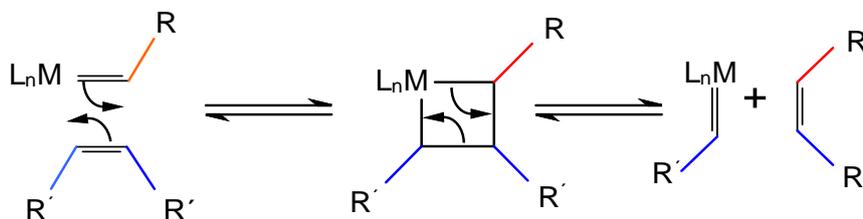


Scheme 1. Alkene metathesis reaction.

Various names are often used for specific types of olefin metathesis depending on the substrate involved in the reaction: (1) cross-metathesis (CM) for reactions between two or more different olefinic substrates, (2) ring-closing metathesis (RCM) for reactions involving dienes that lead to ring formation, (3) acyclic diene metathesis (ADMET) for reactions that lead to linear polyenes, and (4) ring-opening metathesis polymerization (ROMP) for transformations of cycloalkenes into polymers with unsaturated main chains. Because of its general character, olefin metathesis has a wide range of applications in organic synthesis, ranging from the production of fine chemicals (e.g., natural products, biologically active compounds, pharmaceuticals), to large-scale industrial processes (petrochemistry, polymer synthesis). In 2005, Chauvin, Grubbs, and Schrock were awarded the Nobel Prize “for the development

of the metathesis method in organic synthesis". Many important aspects of olefin metathesis and its applications have already been discussed in detail in several monographs [1–4].

Olefin metathesis catalysts are exclusively based on the following transition metals: Ti, Ta, Mo, W, Re, and Ru, however, the importance of Ti and Ta is very limited [5,6]. In addition, carbenes of these transition metals have been shown to act as active catalytic species, which exchange alkylidene molecular fragments through metallacyclobutane intermediates [7] (Scheme 2).

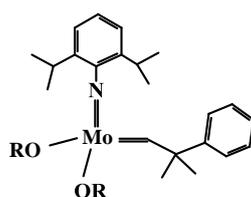


M = transition metal, L_n = ligands at transition metal

Scheme 2. Mechanism of alkene metathesis.

Most metathesis catalysts are water and oxygen sensitive, thus, the metathesis reaction is usually performed under inert conditions. Traditionally, metathesis catalysts are divided into two categories: (a) ill-defined and (b) well-defined catalysts [8]. Ill-defined catalysts (historically older) include catalytic systems in which metallocarbenes are formed “in situ” in a reaction between components of the catalytic system and often the substrate itself. For example, in the formerly popular system WCl_6 + tetraalkyltin, tungsten carbenes are formed “in situ” in a reaction between these two components. Similarly, in industrially used systems based on Mo, W, and Re oxides on silica or alumina supports, active metallocarbenes are formed during the activation process involving substrate molecules [9]. In turn, the group of well-defined catalysts (developed later) includes stable (isolable and storable) metal carbene complexes that can be directly used as catalysts (Schrock W, Mo alkylidene complexes [10], Grubbs Ru carbenes [11]). Typical Schrock and Grubbs carbenes are depicted in Figures 1 and 2, respectively. They are used in organic solvents (usually dried and degassed) as homogeneous catalysts. The first attempts to immobilize these complexes on silica surfaces started soon after their discovery [12,13].

Initially, microporous silica or silica-alumina were used as supports for molybdenum and tungsten oxide catalysts. However, the advantage of mesoporous supports was soon recognized. Ookoshi and Onaka [14] studied 1-octene metathesis over MoO_3 supported either on commercially available silica (Brunauer-Emmett-Teller (BET) area $619 \text{ m}^2/\text{g}$) or on laboratory prepared hexagonal mesoporous silicas (HMS) (d_{100} spacing $\geq 3 \text{ nm}$, BET areas between 1230 and $1450 \text{ m}^2/\text{g}$). The differences in both reaction rates and yields of the reactions were enormous. Over low-surface silica, metathesis products were formed in negligible amounts, whereas HMS provided yields up to 45%. In the same reaction, Topka et al. [15] similarly observed that the activity of MoO_3 supported on the mesoporous molecular sieves MCM-41, MCM-48, and Santa Barbara Amorphous (SBA-15) was higher than that of MoO_3 on conventional silica. This enhanced activity was ascribed to better MoO_3 dispersion on supports with larger surface areas.



$R = t\text{-Bu}$ (3.1), $CMe_2(CF_3)$ (3.2), $CMe(CF_3)_2$ (3.3), and $C(CF_3)_3$ (3.4)

Figure 1. Typical Schrock carbenes.

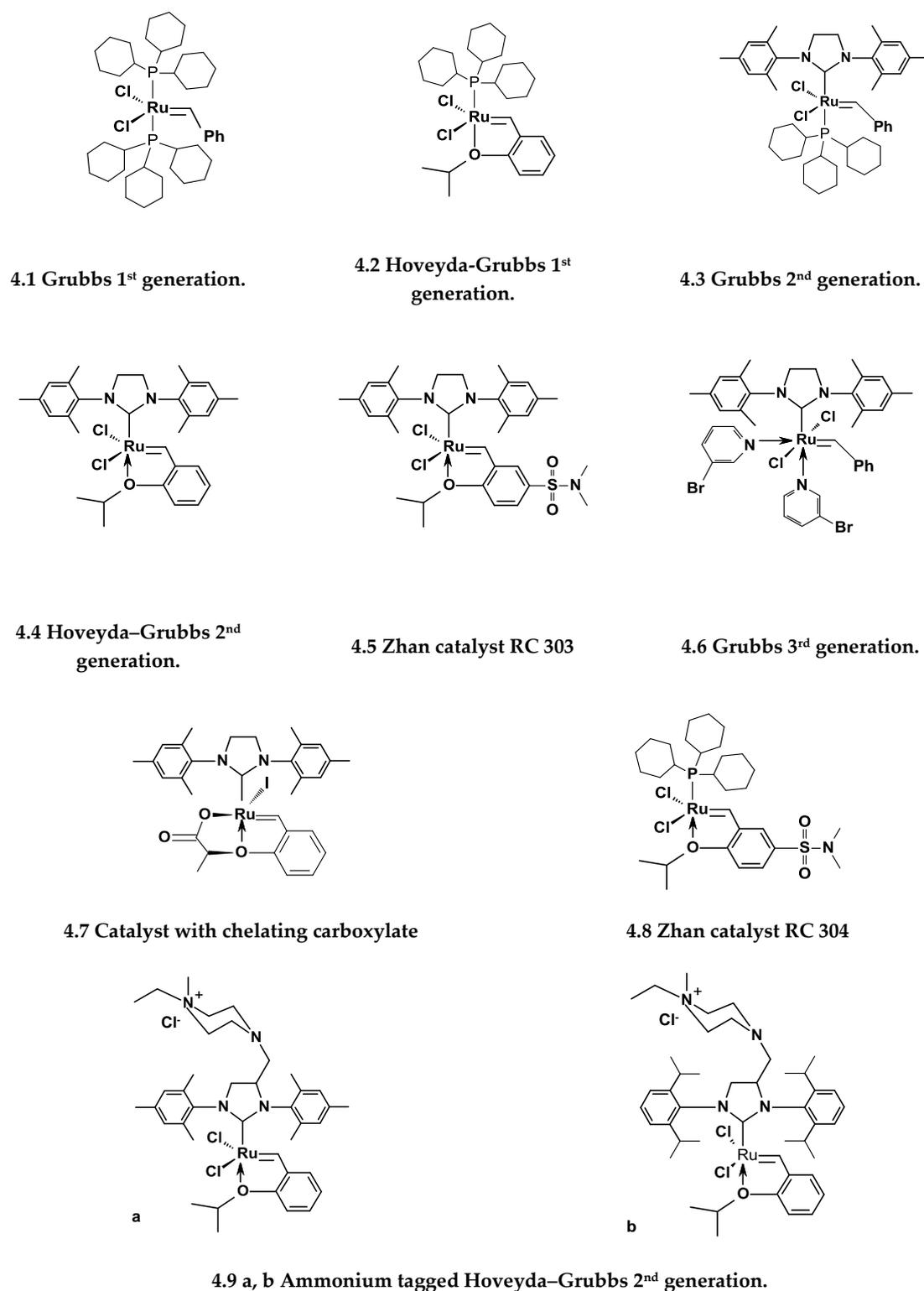


Figure 2. Typical Grubbs-, and Hoveyda-Grubbs-type carbenes used in hybrid catalyst.

The immobilization of Schrock and Grubbs complexes on solid supports aimed (i) to increase catalyst stability (especially by preventing bimolecular decomposition reactions), (ii) to improve catalyst separation from the reaction mixture, and (iii) to reuse the catalyst. The mesoporous character of the supports makes it possible to introduce rather bulky complexes into the pores and facilitates the access of substrate molecules to the catalytic centers. The confinement of catalysts in pores of different sizes

and shapes was also predicted to generate corresponding changes in catalyst selectivity. Therefore, various mesoporous sieves were used as supports to immobilize Schrock and Grubbs catalysts with varying degrees of success [16,17].

Santa Barbara Amorphous (SBA-15) [18] is a mesoporous silica with unique properties that allow its application as an advanced support for metathesis catalysts: uniform, hexagonally-ordered cylindrical mesopores (*p6mm* symmetry group), thick amorphous walls (3–6 nm [19]), hydrothermal stability, large BET areas ($S_{\text{BET}} = 500\text{--}900 \text{ m}^2/\text{g}$), and large pore volume (up to $1.0 \text{ cm}^3/\text{g}$) [20]. The external surface area is usually 10% or less of the total surface [15,20]. Therefore, most of the area available for catalyst accommodation is in the mesopores.

The mesopore diameter depends on the preparation method and typically ranges from 6 to 10 nm, although large-pore SBA-15 with a pore diameter up to 18 nm have been prepared using special swelling agents [19,21]. Such pores facilitate the placement of metathesis catalysts on the inner surface of SBA-15: for example, Hoveyda–Grubbs 2nd-generation catalyst 4.4 (see Figure 2) has a molecular size of $1.76 \times 1.35 \times 1.05 \text{ nm}$ [22], and substrate diffusion to the catalytic centers cause no serious hindrance to the reaction. Nevertheless, the existence of U-shaped mesopores was proven by Transition Electron Microscopy (TEM) [23] in large SBA-15 particles, which may have a negative effect on diffusion in the pores. Moreover, in many SBA-15 particles, micropores were observed in the walls, the amount, however, can be affected by template composition and by the calcination procedure [19].

The attachment of transition metal carbenes or their precursors on the surface can proceed in two ways: (1) by direct reaction with surface OH groups and (2) by functionalization of the surface with linkers, that is, special molecules designed for binding the support surface and the metal carbene (or its precursor). In both ways, the character and amount of surface OH groups are essential. In all-siliceous SBA-15, OH groups are weakly acidic (pK_a about 4 [24]), and their amount depends on the preparation protocol and on the temperature treatment. For SBA-15 calcined at $550 \text{ }^\circ\text{C}$, the number of silanol groups accessible to pyridine molecules (determined by NMR) initially reported was 3.7 groups per nm^2 [24]. Later, van der Voort et al. [25] reported a total amount of OH groups in SBA-15 determined by IR of 3.5 mmol/g. However, a considerable part of these groups is buried in walls and inaccessible to reagents. The reported amount of OH groups capable of being grafted with trimethylsilyl groups is 1.8 mmol/g, which gives 1.7 OH group per nm^2 , with a slightly lower value (1.2 OH group per nm^2) for the often used hexagonal MCM-41 and cubic MCM-48 particles with narrower pore sizes (2.9 and 2.8 nm of diameter, respectively). At high temperatures, when partial dehydroxylation occurs, the amounts of OH groups decrease. Thus, 1.56 mmol of accessible silanols per gram was reported for SBA-15 partially dehydroxylated at $500 \text{ }^\circ\text{C}$ in vacuo [26], and the amount of available OH groups dropped to 1.07 mmol/g for SBA-15 dehydroxylated at $700 \text{ }^\circ\text{C}$ [27]. In this case, entirely isolated OH groups occur on the surface, and they can be used to prepare “single-site catalysts” via methods of surface organometallic chemistry [28].

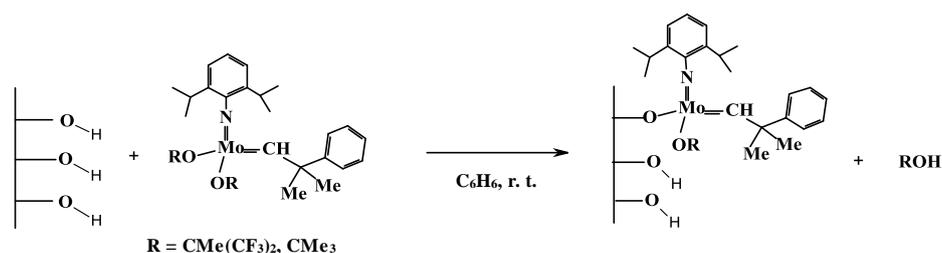
2. Well-Defined Heterogeneous Olefin Metathesis Catalysts Prepared by Immobilization of Mo and Ru Organometallic Complexes on SBA-15

These catalysts combining inorganic support and organometallic catalysts are also known as hybrid catalysts. Well-defined olefin metathesis catalysts, i.e., Schrock and Grubbs-type carbenes were immobilized on various types of silica or silica-alumina supports ranging from high-surface microporous silica through mesoporous molecular sieves to micro- or mesoporous zeolites. Microporous silica was the most common type at first, but advances in the development of organized mesoporous silica (especially mesoporous molecular sieves MCM-41, MCM-48, and SBA-15) led to the increased number of applications of these materials as advanced supports. Recently, new types of zeolites (mesoporous, two-dimensional [29–31]) have been shown to be interesting supports for new metathesis heterogeneous catalysts (vide infra). Several review articles and book chapters have been devoted to this topic [16,17,32–36] and therefore we have exclusively focused on catalysts with a SBA-15 support and on their state-of-the-art features.

Generally, transition metal carbene complexes can be attached to silica supports by a) covalent bonds and b) non-covalent interactions. The following strategies have been developed for this immobilization: (1) direct grafting of the complex on the support through a reaction of ligands of the carbene complex with silanol groups, (2) attachment of the complex through linkers, i.e., molecules with a trialkoxysilyl group that is able to react with silanol groups of the support on one side and with a reactive group that is able to coordinate a metal in the complex (e.g., amino, phosphino, carboxylate) on the opposite site – although this method is more material and time consuming than the others, it ensures some distance between the complex and the channel wall (proximity to the surface may affect the catalytic activity of the immobilized carbene complex [37]), and (3) attachment via non-covalent interactions (ionic, hydrogen bond) – this approach has become particularly important in connection with specific Grubbs-type complexes (vide infra).

Stability is the key characteristic of every catalyst. In the case of hybrid catalysts, this means not only is high Turnover number (TON) achievable but there is also catalyst reusability and no leaching of metal (or other catalyst residues) into the reaction medium. A good catalyst should be reusable many times with no decrease in its catalytic activity, and transition metal leaching must be negligible (no additional purification of products from metal or other catalyst residues is needed, especially for pharmaceutical compounds). Such a good catalyst can also be applicable in flow systems. Unfortunately, the application of well-defined heterogeneous catalysts in flow reactors is still rather rare, and data on leaching and reusing are unavailable for many catalysts reported in literature.

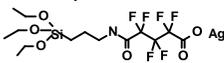
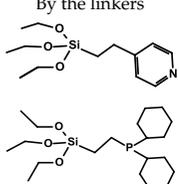
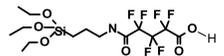
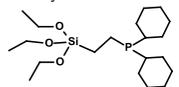
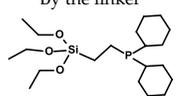
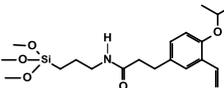
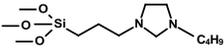
Schrock carbene complexes **3.1** and **3.3** Mo(=CHCMe₂Ph)(=N-2,6-*i*-Pr₂C₆H₃)(OR)₂ (R = CMe₃, CMe(CF₃)₂) were grafted on dehydrated mesoporous molecular sieves MCM-41, MCM-48, and SBA-15 via exchange of alkoxy ligands with surface hydroxyls (Scheme 3) [38]. Hybrid catalysts with 1 wt% Mo have been prepared. The resulting alcohols were detected by gas chromatography (GC), albeit without determining their quantity, so the complexes could be bound to the surface by one or two Mo-O-Si-bond(s). In metathesis of neat 1-heptene, the hybrid catalysts exhibited good activity, slightly increasing in the following order: MCM-48 < MCM-41 < SBA-15 (batch reactor, TON ranging from 1300 to 1700) with negligible Mo leaching. In comparison, the same complexes immobilized on dehydroxylated silica [39] gave monosiloxy surface complexes with a well-determined structure and with high activity in propene metathesis (flow reactor, TON about 188,000) and in a metathesis of methyl oleate (batch reactor, equilibrium after 24 h and TON = 2000).



Scheme 3. Grafting of Schrock alkylidenes **3.3** and **3.1** on mesoporous molecular sieves.

Ru carbenes (Grubbs- and Hoveyda–Grubbs-type) have been immobilized on mesoporous molecular sieves (and especially on SBA-15) more frequently than Schrock-type alkylidenes. A possible reason is that Ru carbenes are not as oxygen- and moisture-sensitive as Schrock alkylidenes and therefore their protection by inert atmosphere during immobilization need not be so rigorous. Some of these catalysts operate even in a water environment, so they can be applied in the metathesis of water-soluble substrates. The main strategies for the immobilization of Ru carbenes on inorganic supports are summarized in References [40,41]. Table 1 outlines Ru carbenes immobilized on SBA-15. Their immobilization approach is indicated together with their main characteristics.

Table 1. Survey of Ru carbenes immobilized on Santa Barbara Amorphous (SBA-15)

Number	Carbene Complex	Immobilization Mode	Loading, in wt % Ru	Activity	Leaching in % of Starting Amount of Ru	Reusing	Reference
1	4.4 4.5	By the linker 	0.85% 0.65%	TON in RCM = 2900	2.3%	3 times	[42]
2	4.3 4.6	By the linkers 	0.3–1.0%	TON in RCM = 2000	0.18–7.7%	6 times	[43]
3	4.7	By the linker 	0.27%	TON in RCM = 2100	2.7%	5 times	[44]
4	4.8	By the linker 	1.07%	RCM, ROMP	0.1–0.38%	6 times	[45]
5	4.8	By the linker 	0.3%	Metathesis and cross-metathesis of cardanol, TON up to 330	0.5%	5 times cumulative TON = 1125	[46]
6	4.2 4.4		0.5–1.7%	RCM TON = 20 in 1 cycle	6–30% according to pore size	8 times	[47]
7	4.1		-	RCM TON = 20 in 1 cycle.	below detection limit	5 times	[48]
8	4.4 4.5	Linker free	0.29–1.0%	TON up to 600 batch reactor	0.04% in C ₆ H ₁₂ , 14% in DCM	Flow conditions possible	[49–53]
9	4.4	By means of Al modification of the surface	1.5%	Cumulative TON about 3000 (propene metathesis)	Catalyst leaches in polar medium	-	[54]
10	4.9a	Linker free	1.2%	TON up to 3300 in RCM	About 1% in DCM and EtOAc	5 times	[55]
11	4.9b	Linker free	0.1–1%	TON up to 35000 in RCM, TON = 1600 in cardanol metathesis	About 1%	More than 10 times suitable for flow condition	[56,57]

RCM = ring closing metathesis, ROMP = ring-opening metathesis polymerization, TON = turnover number, DCM = dichloromethane, EtOAc = ethyl acetate.

Immobilization usually proceeded by mixing (or refluxing) the suspension of a support (dehydrated, and/or surface-modified) with the solution of a carbene complex in an inert atmosphere. After a given time, the solid catalyst was isolated (by decantation, filtration, centrifugation), washed, and dried. The support architecture and main texture characteristics were preserved. Only a decrease in S_{BET} area was found in almost all cases. As examples, the N_2 adsorption isotherms of SBA-15, **4.4** and **4.5** carbenes immobilized on SBA-15 using hexafluorocarboxylate linker—Table 1, entry 1 (denoted as **4.4/SBA-15** and **4.5/SBA-15**) are displayed in Figure 3. The S_{BET} areas (m^2/g), void volumes (cm^3/g), and pore diameter (nm) were 829, 1.18, and 6.6 for the parent SBA-15, 585, 0.98, and 6.5 for **4.4/SBA-15**, and 591, 0.97, and 6.5 for **4.5/SBA-15**. Similarly, **4.1** immobilization on SBA-15 using an N-heterocyclic carbene (NHC) linker (Table 1, entry 7) led to a decrease in S_{BET} from 734 to 233 m^2/g and in pore size from 7.4 to 5.2 nm, thus highlighting that the mesoporous character was preserved [48]. The preservation of the SBA-15 structure in the corresponding hybrid catalysts was also clearly shown by TEM [47,48].

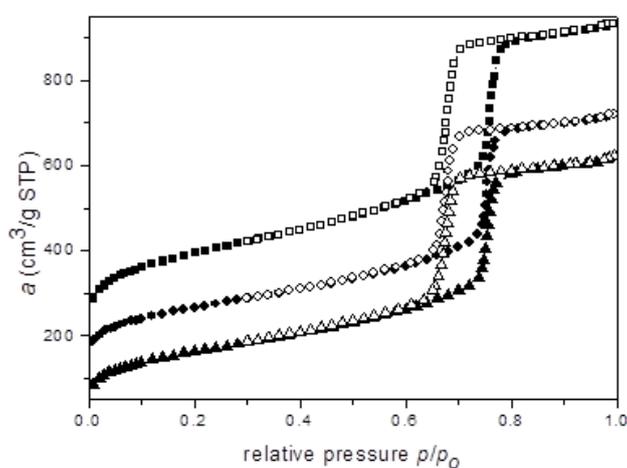


Figure 3. Nitrogen sorption isotherms of the parent SBA-15 (square), **4.4/SBA-15** (circle), and **4.5/SBA-15** (triangle). Adsorption branch filled, desorption branch open points. For clarity, 100 and 150 cm^3/g (Standard Temperature and Pressure) was added to the isotherms of **4.5/SBA-15** and SBA-15, respectively. Taken from Reference [42]—© Springer. Reproduced with the permission of Springer.

In some cases, OH groups remaining on the surface after its functionalization by linkers were covered with Me_3Si groups usually using trimethylchlorosilane or hexamethyldisilazane. This prevents these OH groups from reacting with Ru complexes, and/or with the substrate and increases the hydrophobicity of the surface [42]. Selective capping of OH groups on the external surface (before linker and/or Ru complex application) [48,58] was used to introduce catalytically active Ru species exclusively into the support channels.

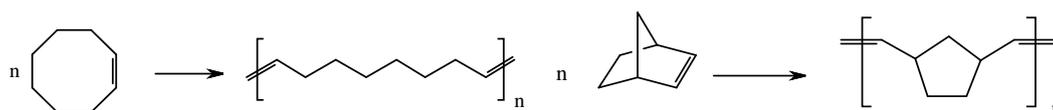
The bond between the NHC linker and the Ru atom (Table 1, entry 7) is very stable. Therefore, the hybrid catalyst is reusable, and Ru leaching into liquid phase is negligible. Similarly, carboxylate linkage (Table 1, entries 1 and 3) is sufficiently firm. However, in both cases, several step synthesis procedures are necessary for linker preparation. On the other hand, pyridine and phosphine linkers are commercially available, and the preparation of hybrid catalysts with them is easy (Table 1, entries 2, 4, 5). Nevertheless, the catalytic reaction starts with pyridine or phosphine ligand dissociation, thereby vacating a place for substrate coordination. This suggests that the catalytically active Ru species are not bound to the surface during the whole catalytic cycle. The reusability of the corresponding hybrid catalysts, low Ru leaching, and split (filtration) tests, which have confirmed the reaction heterogeneity [59], have been explained based on the notion that catalytically active Ru species are captured by free linkers during their movement in the channels and that this dissociation-re-capturing process is repeated many times during the reaction [43]. The immobilization of Hoveyda–Grubbs

carbenes using an isopropoxystyrene linker (Table 1, entry 6) is associated with a similar problem: in the first metathesis step, this isopropoxy styrene ligand must be replaced by an alkylidene from a substrate according to the general mechanism of metathesis (see Scheme 2) and therefore the catalytic centres will lose their bond with the surface. This explains the relatively high catalyst leaching, which increases with the pore size [47].

“Linker free” immobilization of Hoveyda–Grubbs 2nd-generation carbenes on silica materials including SBA-15 (Table 1, entry 8) is a very advantageous method for the preparation of hybrid metathesis catalysts based on a simple mixing of a carbene solution and a silica support. This method was first described by Sels et al. [49], and the catalysts prepared using this approach turned out to be very active in all types of metathesis reactions. When used in a non-polar medium (e.g., cyclohexane), they behaved as true heterogeneous catalysts: they were reusable with very low Ru leaching and applicable in flow reactors as well. Hoveyda–Grubbs 2nd-generation carbenes with ionic tags (4.9a, b) provide hybrid catalysts that also work in polar solvents such as dichloromethane or ethyl acetate and that are highly active in the metathesis of various substrates (Table 1, entries 10, 11). Considering their stability, activity, and selectivity, these catalysts are among the best hybrid metathesis catalysts. An in-depth understanding of non-covalent interactions between the carbene complex and the support in these catalysts remains elusive. Although originally described as physisorption, the strength of this bond suggests that stronger interactions, similar to hydrogen bonds, must come into play. In this context, the immobilization of Hoveyda–Grubbs 2nd-generation carbene on SBA-15 with an Al-modified surface (Table 1, entry 9) with the proposed Al-Cl-Ru bond is inspiring.

3. Application of SBA-15-Based Hybrid Catalysts in Metathesis Polymerization Reactions

Metathesis polymerization reactions (ADMET polymerization and ROMP) are still a domain of homogeneous catalysts. Nevertheless, several successful attempts to use hybrid metathesis catalysts in ROMP are noteworthy. The Schrock Mo-alkylidene complex 3.3 grafted on SBA-15 (3.3/SBA-15) has been used in a ROMP of cyclooctene (COE) and norbornene (NBE) (Scheme 4) and delivered a poly(COE) of $M_w = 210,000$ in 87% yield and a poly(NBE) of $M_w = 1,800,000$ in 60% yield [38]. During polymerization, the resulting polymers were continuously released into the liquid phase due to chain transfer by the polymer. The molecular weight of the polymer could be effectively reduced by adding 1-heptene as a chain transfer agent. The content of Mo in the isolated polymer was 6 ppm [60].



Scheme 4. Ring-opening metathesis polymerization (ROMP) of cyclooctene and norbornene.

The Ru carbene precursors $(\text{RuCl}_2(p\text{-cymene}))_2$ and $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$, where Cy = cyclohexane, immobilized on SBA-15 provided high-molecular weight poly(NBE) in high yields (in the former, after activation with (trimethylsilyl)diazomethane) [61,62]. Ru carbene 4.5 immobilized on SBA-15 via carboxylate linker produced a poly(COE) of $M_w = 230,000$ and a poly(NBE) of $M_w = 2,200,000$. The Ru content of the polymer was 16 ppm [42]. The same carbene complex 4.5 immobilized in “linker-free” mode was applied in ROMP of COE, yielding a polymer of $M_w = 330,000$ [51]. Large-pore supports were necessary for high polymer yields (Figure 4): the highest yield was obtained over a hybrid catalyst using an SBA-15 with a pore size of 11.1 nm. Conversely, the premature end of this polymerization over a catalyst on ordinary silica particles suggests that the narrow pores are blocked by growing polymer chains.

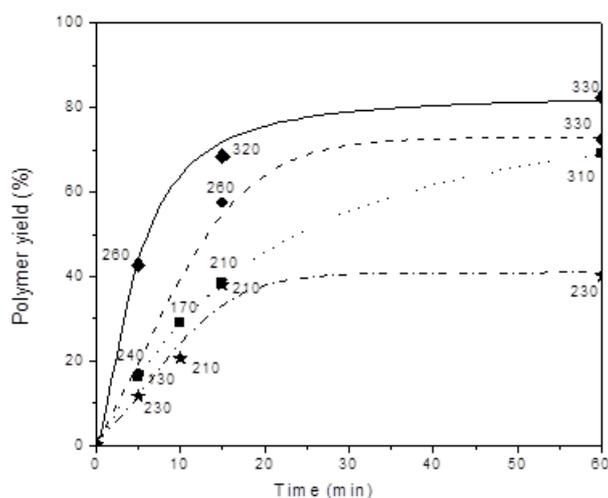


Figure 4. ROMP of cyclooctene over 4.5/SiO₂ (stars), 4.5/MCM-41 (squares), 4.5/SBA-15 d = 6.3 nm (circles), 4.5/SBA-15 d = 11.1 nm (diamonds). Cyclohexane, $T = 13\text{ }^{\circ}\text{C}$, molar ratio cyclooctene/Ru = 500, $c^0_{\text{cyclooctene}} = 0.6\text{ mol/L}$, numbers at individual experimental points give M_w of polymer in thousands. Taken from Reference [51] ©Elsevier. Reproduced with the permission of Elsevier.

In all cases, polymerization over hybrid catalysts provided polymers with a high polydispersity index ($M_w/M_n > 2$), which is most likely associated with the slow reaction initiation and with the intensive chain transfer. The main advantage of applying a hybrid catalyst was the easy separation of polymers from catalysts and the preparation of polymers with a very low content of catalyst residues without requiring additional purification. The catalysts, however, were not reused.

4. Heterogeneous Olefin Metathesis Catalysts Consisting of Mo and W Oxides on SBA-15

MoO₃ and WO₃ deposited on silica or silica–alumina supports are some of the earliest metathesis catalysts. These relatively inexpensive catalysts are widely used, especially in large-scale petrochemical processes. With the discovery of new advanced supports, such as zeolites and mesoporous molecular sieves, molybdenum and tungsten oxides particularly attracted the attention of many research groups in their efforts to increase the effectiveness of commercially important catalysts [9,63]. Several studies showed that various mesoporous siliceous materials (MCM-41 [15,64,65], KIT-6 [66]), or MWW-zeolites [65,67], and MFI-zeolites [65,67,68] were substantially more active than ordinary silica or silica-alumina. However, the most commonly used support was SBA-15 for its large pores and high BET areas. Table 2 outlines catalysts based on molybdenum and tungsten oxides supported on SBA-15.

Table 2. Survey of Mo and W oxide catalysts supported on SBA-15.

Number	WO _x , MoO _x Species Source	Method of Catalyst Preparation	W, Mo Loading Wt %	Substrate	Activity	Reference
1	MoO ₃	thermal spreading	4–12	1-octene	TOF = 0.003 mol/mol _{Mo} ·s at 40 °C	[15]
2	ammonium heptamolybdate (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	ion exchange	10.1	-	-	[69]
3	ammonium heptamolybdate (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	ion exchange	9.7	propene	TOF = 2.06 mmol/mol _{Mo} ·s at 50 °C	[70]
4	ammonium heptamolybdate (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	wet impregnation	3	1-butene	60% conversion at 450 °C	[71]
5	MoO ₂ (acac) ₂ MoO ₂ (gly) ₂	thermal spreading, wet impregnation	4–12	1-octene, 1-dodecene, 1-tetradecene	TOF = 0.008 mol _{1-oct} /mol _{Mo} ·s at 40 °C	[72]
6	MoO ₃ , MoO ₂ (acac) ₂	thermal spreading	6	2-pentene	40% conversion at 500 °C	[65]

Table 2. Cont.

Number	WO _x , MoO _x Species Source	Method of Catalyst Preparation	W, Mo Loading Wt %	Substrate	Activity	Reference
7	ammonium heptamolybdate (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	direct co- condensation	1.3–10.8	1-butene	65% conversion at 450 °C	[71]
8	ammonium heptamolybdate (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	wet impregnation on alumina- modified surface	ca. 6	1-butene	65% conversion at 90 °C	[73]
9	ammonium metatungstate (NH ₄) ₆ H ₂ W ₁₂ O ₄₀ ·xH ₂ O	wet impregnation	10 wt% of WO ₃ (8% of W)	2-butene	75% conversion at 550 °C	[64]
10	Sodium tungstate NaWO ₄ ·2H ₂ O	direct co- condensation	5% and 9% of WO ₃	2-butene	87% conversion at 550 °C	[64,74]
11	ammonium metatungstate (NH ₄) ₆ H ₂ W ₁₂ O ₄₀ ·xH ₂ O	wet impregnation	6	2-pentene	56.5% conversion at 550 °C	[65]
12	Sodium tungstate NaWO ₄ ·2H ₂ O	direct co- condensation	Si/W=35	1-butene	92% conversion at 350 °C	[75,76]

acac = acetylacetonate, gly = glycolate, TOF = turnover frequency.

In principal, the catalysts were prepared using the following approaches: (a) thermal spreading, (b) wet impregnation, (c) ion exchange, and (d) hydrothermal direct co-condensation. (a) Thermal spreading is a very simple method consisting of heating a physical mixture of SBA-15 and the source of Mo to 500 °C for several hours in air (Table 2, entries 1, 5, 6). (b) SBA-15 impregnation with an appropriate amount of a water solution of Mo or W compound followed by drying and calcination is a commonly used method for wet impregnation (Table 2, entries 4, 5, 8, 9, 11). (c) In the ion exchange method (Table 2, entries 2, 3), SBA-15 is modified by a reaction with trimethoxysilylpropylamine and then with HCl, followed by anion exchange with ammonium heptamolybdate in water. During calcination, the organic parts are removed, and MoO_x species remain on the supports. According to the authors, this method provides a better control of the dispersion of Mo species on the surface than wet impregnation [77]. In all previous catalysts given in (a), (b), and (c), the mesoporous structure of the SBA-15 support was preserved. (d) The direct co-condensation method was used for the synthesis of Mo- and W-containing silica materials by adding a metal oxide source to the mixture for the hydrothermal preparation of SBA-15. Characterization using current physico-chemical methods showed that the resulting materials had hexagonal channels and textural parameters similar to SBA-15 and Mo- or W-oxide species dispersed in the silica framework (Table 2, entries 7, 10, 12).

All these systems are typical “ill-defined” catalysts. The real catalytically active centres are surface carbenes, which are formed “in situ” from their closest precursors on the surface and from substrate molecules. The number of surface carbenes was estimated as 2% of the original metal content [70]. The formation of the closest precursors of surface carbenes proceeds during the activation process (heating the catalyst to approximately 500 °C, usually in an inert atmosphere). Under the same conditions, catalysts are often regenerated. Isolated (-O-)₂M(=O)₂ species are usually considered the closest precursors of surface carbenes and therefore perfect dispersion of the metal oxide along the surface is an essential condition for catalyst activity [9,70,78]. In this regard, the high BET area of SBA-15 is an important advantage.

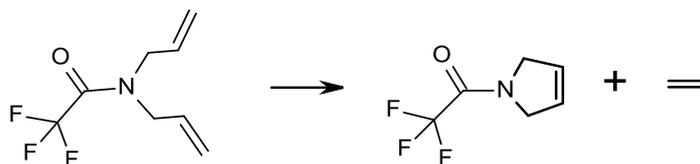
The experimental work in this field was accompanied by a computational approach to the study with the aim to describe the surface process on a molecular level and to help in understanding the role of support [79]. In computational studies of Mo oxide species on silica surface DFT methods were usually used and silica support was approximated by a structure similar to β-cristobalite [80–82].

Catalytic activity depends on the (a) characteristics of the support (its texture parameters and acidity), (b) method of metal deposition and metal loading, (c) parameters of the activation process, (d) quality of the substrate, and (e) reaction conditions. This high number of variables complicates any comparison between activity data from different sources. Nevertheless, some general remarks can be made. (i) The acidity of the supports presumably increases the activity of the catalyst. The beneficial effect of Al modification of the SBA-15 (Table 2, entry 8) was ascribed to the formation of Brønsted acid sites, which improve Mo dispersion. Conversely, acidity induces double bond isomerization

and alkene oligomerization [67]. (ii) The dependence of activity on metal loading has a maximum: at high metal concentrations, the dispersion is imperfect, and a part of the metal forms metal oxide microcrystals, which do not contribute to the catalytic activity. The optimal metal loading usually ranges from 4 wt% to 8 wt% of the metal [72]. (iii) Mo catalysts usually operate at lower temperatures than W catalysts. In some cases (Table 2, entries 1, 3, 5, 8), Mo catalysts were active at temperatures below 100 °C. (iv) In most cases, Mo and W oxide catalysts were used in the metathesis of light olefins. Nevertheless, these catalysts were also active in the metathesis of longer chain alkenes C₈–C₁₄ (Table 2, entries 1 and 5).

5. Comparison of SBA-Based Olefin Metathesis Catalyst with Catalysts using other Advanced Supports (Mesoporous Molecular Sieves and Zeolites)

Systematic studies comparing the activity of catalysts based on SBA-15 with that of catalysts using other mesoporous molecular sieves and/or zeolites under the same conditions are rather rare. Most existing reports focus on Ru hybrid catalysts. Using phosphine linkers, Hoveyda–Grubbs-type carbene **4.8** was immobilized on several all-siliceous mesoporous molecular sieves differing in architecture and pore size: (i) hexagonal channel-like MCM-41 ($S_{\text{BET}} = 972 \text{ m}^2/\text{g}$, $d = 4.0 \text{ nm}$), (ii) SBA-15 ($S_{\text{BET}} = 766 \text{ m}^2/\text{g}$, $d = 6.2 \text{ nm}$), (iii) cubic three-dimensional (3D) pore-like MCM-48 ($S_{\text{BET}} = 756 \text{ m}^2/\text{g}$, $d = 6.0 \text{ nm}$), and (iv) cubic cage-like SBA-16 ($S_{\text{BET}} = 796 \text{ m}^2/\text{g}$, $d_{\text{entrance}} = 4.7 \text{ nm}$). In RCM of N,N-diallyl-2,2,2-trifluoroacetamide (DAF) (Scheme 5), the initial reaction rate and/or conversion achieved increased with the pore size of the catalyst support in the following order: MCM-41 < SBA-16 < MCM-48 < SBA-15 (Figure 5). This suggests that the increased diffusion in the pores positively affects the reaction rate [45]. Nevertheless, the reaction rate of the catalyst on SBA-15 is still significantly lower than that of **4.8** used as a homogeneous catalyst. Thus, the advantages of hybrid catalysts are limited to easy product separation and catalyst reusability.



Scheme 5. Ring-closing metathesis (RCM) of N,N-diallyl-2,2,2-trifluoroacetamide.

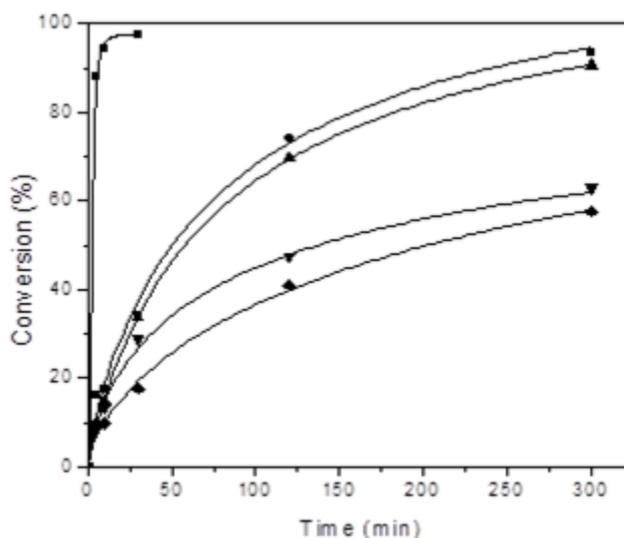
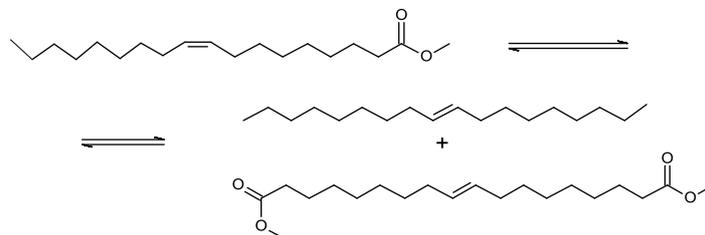


Figure 5. RCM of N,N-diallyl-2,2,2-trifluoroacetamide (DAF) with catalysts **4.8** (■), **4.8**/SBA-15 (●), **4.8**/MCM-48 (▲), **4.8**/SBA-16 (▼), and **4.8**/MCM-41 (◆). 30 °C, Ru/DAF = 1:100, toluene, c⁰ (DAF) = 0.15 mol/L. Taken from Reference [45] ©Elsevier. Reproduced with the permission of Elsevier.

Similar effects of support pore size on the reaction rate were observed in metathesis of methyl oleate (Scheme 6) over **4.6** immobilized by phosphine linkers on MCM-41 ($d = 4.0$), and two SBA-15 supports with different pore diameters ($d = 6.9$ and $d = 11.1$): the reaction rates (at inflexion points of conversion curves) increased with the pore size (Figure 6) [43].



Scheme 6. Metathesis of methyl oleate.

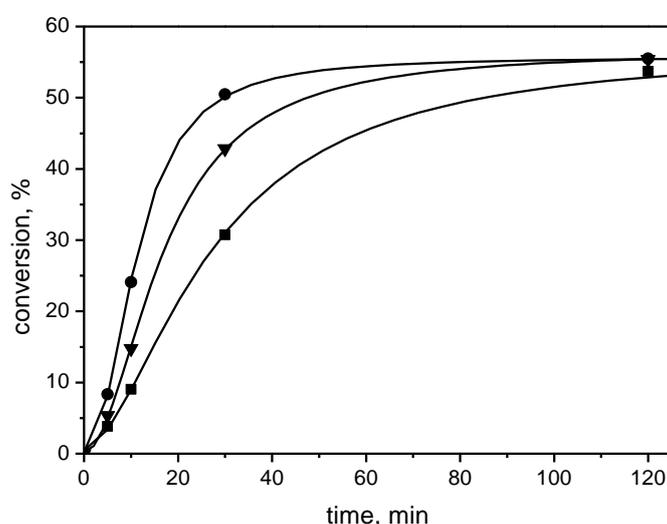


Figure 6. Effect of catalyst pore size on conversion in the metathesis of methyl oleate. Toluene, 60 °C, Ru/MeOI = 1:250, $c_{\text{MeOI}}^0 = 0.15$ mol/L, catalysts **4.6**/SBA-15 ($d = 6.9$ nm) (▼), **4.6**/SBA-15LP ($d = 11.1$ nm) (●), **4.6**/MCM-41 (4.0 nm) (■). Taken from Reference [43] © American Chemical Society (ACS). Reproduced with the permission of ACS Publications.

Similar trends were also reported for linker-free immobilized Hoveyda–Grubbs carbene **4.5**. In RCM of (–)- β -citronellene and metathesis of 1-decene, the initial reaction rates increased with the pore diameter in the following order: **4.5**/MCM-41 ($d = 4.0$ nm) < **4.5**/MCM-48 ($d = 6.0$ nm) < **4.5**/SBA-15 ($d = 6.9$ nm) < **4.5**/SBA-15LP ($d = 11.1$ nm) [51]. The comparison between SBA-15 particles with the zeolites MCM-22, MCM-36, and MCM-56 as supports for ammonium-tagged carbene **4.9a** is given in Reference [83] for metathesis of methyl oleate (Figure 7). The initial reaction rate of the catalyst based on SBA-15 was higher than that of catalysts based on zeolitic supports.

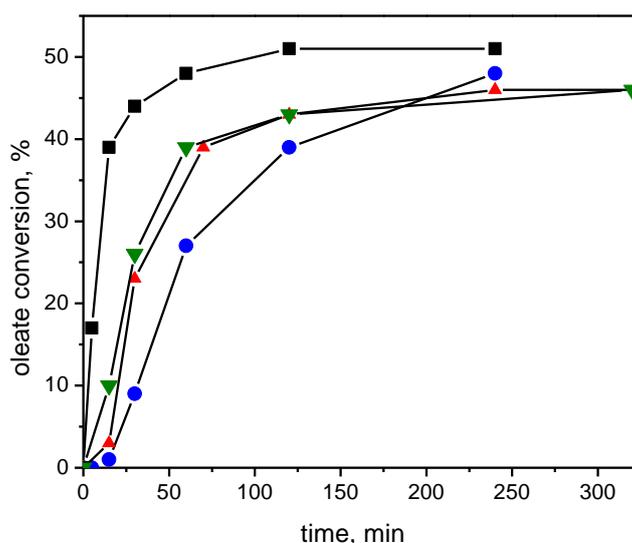
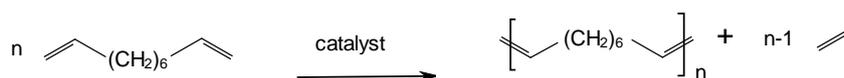
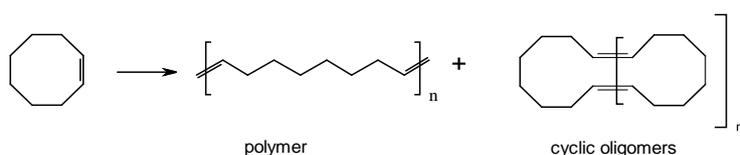


Figure 7. Self-metathesis of methyl oleate over **4.9a**/SBA-15 (■), **4.9a**/MCM-22 (▲), **4.9a**/MCM-56 (▼), and **4.9a**/MCM-36 (●). Toluene, 60 °C, molar ratio oleate/Ru = 250, $c_{\text{MeOl}} = 0.15$ mol/L. Taken from Reference [83].

The characteristics of the support significantly affected not only the activity but also the selectivity of the catalyst. In ADMET of 1,9-decadiene (Scheme 7) over **4.5** on MCM-41 ($d = 4.0$ nm), SBA-15 ($d = 6.9$), and SBA-15LP ($d = 11.1$ nm) [51], the composition of oligomeric products significantly varied with the catalyst support used. When increasing the pore diameter, the selectivity to dimer decreased, and the selectivity to higher oligomer increased. In ring-opening/ring-closing metathesis of cyclooctene (Scheme 8) over **4.4** linker-free immobilized on various supports, the catalysts on SBA-15 and MCM-41 were the most active. However, they strongly differed in selectivity. In the case of SBA-15, the polymer was formed with 45% selectivity. In turn, in the case of MCM-41, no polymer was formed, and higher oligomers (from 6 to 20 monomeric units) prevailed with 65% selectivity [52].



Scheme 7. Acyclic diene metathesis (ADMET) of 1,9-decadiene.



Scheme 8. Ring-opening/ring-closing metathesis of cyclooctene.

In contrast to hybrid Ru catalysts, in which SBA-15 proved its superiority, in oxidic catalysts, i.e., supported MoO_3 and WO_3 , MCM-41 usually gave rise to more active catalysts than SBA-15. An early study on 1-octene metathesis over MoO_3 on mesoporous molecular sieves [15] showed that the activity of $\text{MoO}_3/\text{MCM-41}$ was higher than that of $\text{MoO}_3/\text{SBA-15}$, at least at loadings from 4 wt% to 8 wt% Mo. In 2-pentene metathesis over both Mo and W oxides supported on MCM-41, higher conversions were reached at 500 °C than over catalysts based on SBA-15 despite the larger pore diameter of SBA-15 [65]. Similarly to 2-butene metathesis, the conversion achieved with $\text{WO}_3/\text{MCM-41}$ (8 wt% of W) was higher than that with $\text{WO}_3/\text{SBA-15}$ at all temperatures from 450 to 550 °C [64]. Such results were usually explained as a consequence of the increased specific area and improved oxide dispersion on the surface

of MCM-41. In turn, the metathesis of long chain alkenes (C_{12} , C_{14}) showed better results when using catalysts on SBA-15 [72]. In this case, the advantage of a large pore size prevailed.

6. Conclusions and Perspectives

SBA-15 is an excellent support for metathesis catalysts thanks to its thermal and chemical stability, well-defined structure, and large pores. Especially in hybrid catalysts prepared by immobilization of well-defined Mo and Ru carbenes, these properties have proved particularly useful. Although some Ru carbenes have also been immobilized on other materials such as Metal-Organic Framework MOF [84], graphene [85,86], glass, wool, and paper [87], the data reported so far show that SBA-15 is the most promising support for effective, stable, and widely applicable catalysts.

In our review, we focused on olefin metathesis catalysts using SBA-15 as a support. New metathesis catalysts have been rapidly developed in recent years, and several modern Mo and Ru carbenes are currently available. However, these carbenes were not immobilized at all or were immobilized on current silica only. This remains a great challenge, especially the immobilization of new carbenes with high stereoselectivity [88] and even enantioselectivity [89] as homogeneous catalysts. Another major challenge is the development of heterogeneous catalysts for alkyne and enyne metathesis. For example, Buchmeiser has recently developed silica-supported NHC Mo alkylidyne complexes used in the metathesis of various 2-alkynes [90]. For development of these new hybrid catalysts highly effective in metathesis of a variety of substrates, SBA-15 can be a good choice.

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