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Silica and zirconia supported olefin metathesis pre-catalysts: Synthesis, catalytic activity and multiple-use in dimethyl carbonate

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1. Introduction

The development of clean catalytic processes has known an increasing importance in the context of sustainable production and in green chemistry [1]. In particular, olefin metathesis [2] is a very powerful tool for the efficient catalytic formation of carbon–carbon double bonds allowing the synthesis of various use-ful intermediates and compounds for fine chemistry [3] and for the synthesis of polymers [4]. Amongst ruthenium-based catalysts, Hoveyda-type catalysts have received much attention as homogeneous recyclable catalysts used at laboratory scale as they combine high stability and activity with an excellent tolerance towards polar functional groups [5]. Nevertheless, rather few industrial processes use metathesis reactions owing to the cost of homogeneous catalysts together with difficulties of final separation of the molecular catalysts from the reaction medium and their subsequent

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ABSTRACT

This study is aimed at designing and synthesising new olefin metathesis catalysts grafted onto porous solid supports and using them in dimethyl carbonate (DMC) an eco-friendly solvent. Two hybrid organic–inorganic Hoveyda-type catalysts were prepared in a few steps by initial grafting of a tailor-made ligand by sol–gel process onto porous silica and zirconia. The new hybrid organic–inorganic catalysts were then engaged in a series of model ring closing metathesis reactions (RCM) in the eco-friendly solvent DMC and their multiple-use was studied.

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recycling. To overcome these serious drawbacks that still hamper their industrial scale development, several solutions have been explored. Amongst those are the immobilizations of Hovevda catalysts in non-conventional solvents such as ionic liquids [6], supercritical (Sc) fluids [7] or perfluoroalkanes [8]. Recently, an innovative green process named organic solvent nanofiltration (OSN) has been used for the efficient separation and recovery of homogeneous catalysts at room temperature and without phase change [9]. Previous works from our research group [10] and others [11] implemented OSN for the recovery of tailor-made Hoveyda catalysts. Recently, we also reported an innovative approach for metathesis reactions in a catalytic membrane reactor by immobilization of an ionically tagged Hoveyda catalyst supported in an ionic liquid already impregnated onto a polyimide membrane [12]. The heterogenisation of homogeneous Hoveyda catalyst by immobilization on a porous solid support is the most widely used strategy for recovery and recycling of this type of catalysts [13]. Due to the solid nature of the immobilized catalyst, classical filtration or centrifugation at the end of the metathesis reaction allows for an easy separation of the product and recovery of the catalyst. This immobilization can either be achieved by a covalent bond [14] or by adsorption [15]. More recently, the integration of metathesis reaction using Hoveyda catalyst grafted on porous solid support or on SILP (Supported Ionic Liquid Phase) for continuous flow

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Scheme 1. Synthesis of ligand 6.

process have been reported [16]. The use of eco-friendly solvents in olefin metathesis reactions is another very important parameter to consider in order to decrease its environmental impact. Toluene and dichloromethane are conventional solvents most often used in metathesis reactions, but they have a significant environmental impact owing to their toxicity [17]. In contrast, due to their low toxicity [18,19] dialkyl carbonates are considered as eco-friendly solvents and they have been used in various catalytic transformations [18] including C–H bond functionalisation reactions [20]. In 2008, dimethyl carbonate (DMC) was introduced in olefin metathesis as an alternative to toluene and dichloromethane [21]. Since then it has been used in particular for the transformations of various renewable materials such as methyl oleate or terpenoids [22]. The feasibility of the integration of catalytic olefin metathesis with organic solvent nanofiltration (OSN) in DMC was also recently demonstrated with retention of the organometallic complex similar to those obtained in toluene [10].

The main objective of the present study was to immobilize Hoveyda-type catalysts onto porous silica and zirconia with the aim of studying their catalytic activity and multiple-use capacity in the eco-friendly DMC. As far as we know, this is the first example of immobilization of a Hoveyda-type catalyst onto zirconia that is a less acidic support than silica. Herein, the synthesis of a tailor-made silylated ligand is shown as well as the preparation of hybrid organic-inorganic supported ligand and complexes. Finally, the catalytic activity and reuse of the hybrid catalysts have been evaluated.

2. Results and discussion

2.1. Ligand synthesis

Previous works from different groups showed the influence of aryl substituents of the chelating *o*-isopropoxystyrene ligand on the catalyst efficiency, in particular the initiation step, and on recyclability. For instance, an electron-withdrawing substituent *para* to the isopropoxy group [23] or an *ortho*-substitution of the same isopropoxy group [24] resulted in improved release (initiation) of the ligand thus hampering efficient return considering the boomerang mechanism that was recently ruled out [25]. On the other hand,

Blechert showed that para-substitution with electron donating groups resulted in slower initiation rates [26]. Based on these properties, several catalysts bearing alkyl- or alkoxy-para-substituents have been reported for utilisation in ionic liquids and ScCO₂ [6,8]. Consequently, the synthesis of the new silylated styrene ligand 6 was envisioned for the covalent anchorage of catalytic species onto a solid support (Scheme 1). Ligand 6 was readily synthesized in 5 steps from the commercially available 2,5-dihydroxybenzaldehyde 1. Initial protection of both hydroxyl groups followed by a selective deprotection furnished 2 in 91% yield [27]. Etherification of the residual hydroxyl group led to 3 that was converted into a styrenyl compound **4** by a Wittig olefination. Subsequent alcohol deprotection with sodium methoxide furnished the styrenyl derivative 5 in good yield (85%). Finally, 5 was alkylated with (3iodopropyl)trimethoxysilane in order to introduce the alkoxysilyl group required for anchorage of the ligand onto the solid supports. The reaction performed in DMF afforded the silvlated styrene ligand **6** in 95% purity according to 1 H NMR. Due to its poor stability towards silica gel purification, this product was used without any further purification.

2.2. Preparations of hybrids materials and catalysts

2.2.1. Preparations of hybrids materials

The preparation of two different hybrid materials **M1** and **M2** was carried out via sol–gel grafting of ligand **6** onto silica (Merck, Geduran Si60, $500 \text{ m}^2 \text{ g}^{-1}$) and zirconia (Orelis, $64 \text{ m}^2 \text{ g}^{-1}$) powders, respectively (Scheme 2). The solid supports were initially dried for 24 h at 70 °C under vacuum. The dried solids were added at room temperature to a solution of ligand **6** in dry toluene and refluxed for 24 h. The resulting powders were then washed successively with dichloromethane, diethyl ether and pentane affording **M1** and **M2** as white powders.

In order to evidence the grafting of ligand **6**, **M1** and **M2** powders were studied by ²⁹Si and ¹³C CP-MAS NMR, DRIFT and SEM-EDX. The analysis of the silica powder **M1** by SEM-EDX indicated the presence of the organic silylated ligand **6** on the silica powder by the detection of carbon arising from the organic ligand. The same analysis performed on the zirconia powder **M2** indicated the presence of carbon and silicium arising from ligand **6**. The comparison



Scheme 2. Preparation of hybrid materials M1 and M2.



Fig. 1. DRIFT spectra of virgin silica (black) and hybrid silica material M1 (grey) wavenumber (cm⁻¹).

of the DRIFT spectra of the starting solids with the solids obtained after grafting also evidenced the presence of ligand **6**, as new bands located in the region $1350-1750 \text{ cm}^{-1}$ and $2900-3100 \text{ cm}^{-1}$ were detected with the grafted material **M1** (Fig. 1).

An enlargement of the region $1350-1750 \text{ cm}^{-1}$ showed the presence of four new absorption bands at 1652 cm^{-1} , 1452 cm^{-1} , 1387 cm^{-1} , 1312 cm^{-1} corresponding to $\nu(C=C)$ styrene, $\nu(C=C)$ aromatic, $\delta(CH_3)$ and $\delta(CH_2)$, respectively. Similarly, the region 2900–3100 cm⁻¹ showed two new absorption bands at 2937 cm⁻¹ and 2974 cm⁻¹ attributable to $\nu(CH_3, CH_2)$ asymmetric et $\nu(CH_3, CH_2)$ symmetric. In the case of **M2** new bands also located at 800–1700 cm⁻¹ and 2900–3100 cm⁻¹ appeared (Fig. 2).

In order to confirm the covalent grafting of ligand **6** onto silica and zirconia, solid-state NMR analyses were carried out (Table 1 and Fig. 3).

The ²⁹Si CP-MAS NMR analysis of **M1** confirmed the covalent bonding between the silica support and ligand **6** as T^2 and T^3 subunits [28] were detected in addition to the characteristic Q^2 , Q^3 and Q^4 silica subunits (Fig. 3) [29].

The effect of zirconium second-nearest neighbour on the 29 Si chemical shift is much less documented than silicon or other elements such as aluminium or titanium [30]. The 29 Si CP-MAS NMR analysis of **M2** revealed the appearance of a broad signal centred at -50 ppm. For the reasons mentioned above, this signal was

Table 1

²⁹Si CP-MAS NMR analysis of M1.

Chemical shift (ppm)	-58	-66	-90	-101	-110
SiO _n units	T ²	T ³	Q ²	Q ³	Q^4



Fig. 2. DRIFT spectra of virgin zirconia (black) and hybrid zirconia material $M2({\rm grey})$ wavenumber $({\rm cm}^{-1}).$



Fig. 3. Solid-state ²⁹Si CP-MAS NMR spectrum of hybrid material M1.

attributed to the formation of Si–O–Zr linkage although this cannot be unambiguously determined (Fig. 4).

Finally, the ¹³C CP-MAS NMR spectra of **M1** and **M2** exhibited chemical shifts characteristic of the grafted organic ligand **6**



Fig. 4. Solid-state ²⁹Si CP-MAS NMR spectrum of hybrid material M2.



Fig. 5. Solid-state ¹³C CP-MAS NMR spectrum of hybrid material M1.

(Figs. 5 and 6). Of note, residual methoxy groups were detected at 50 ppm for **M1** whereas they were not observed for **M2**. This may be explained by a higher condensation in **M2** or by a different chemical shift of the methoxy group for **M1** (*Me*OSiOSi) than for **M2** (*Me*OSiOZr).

2.2.2. Preparation of supported catalysts

The new supported Hoveyda-type catalysts **C1** and **C2** were prepared by reaction of the second generation Grubbs catalyst with **M1** or **M2** powders in refluxing CH_2Cl_2 for 12 h. After washing and drying, the solids were obtained as pale green powders thus indicating the formation of the desired supported catalysts (Scheme 3) [31]. To the best of our knowledge, catalyst **C2** is the first example of an homogeneous Hoveyda-type catalyst grafted onto a zirconia support.

The new powders **C1** and **C2** were analysed by the same analytical techniques as for the hybrid materials **M1** and **M2** in order to evidence the formation of the desired supported catalysts.

The analysis of **C1** by SEM-EDX revealed the presence of ruthenium and chlorine thus suggesting the formation of the expected complex. The DRIFT analysis of **C1** confirmed the formation of the desired complex as the intensity of the styrene vibration v(C=C) at 1652 cm⁻¹ decreased due to coordination to the ruthenium (Fig. 7).

In the case of the hybrid catalyst **C2**, due to the small amount of grafted ruthenium species (see below), no noticeable difference could be detected between the virgin hybrid material **M2** and the targeted supported catalyst **C2** by SEM-EDX (precision is close to 5 atom% for each element).

The supported catalysts **C1** and **C2** were then analysed by ²⁹Si CP-MAS NMR and their respective spectra were identical to those of **M1** and **M2** thus demonstrating the stability of the inorganic matrix during the consecutive grafting reactions. The ¹³C CP-MAS NMR spectra of the supported catalysts **C1** and **C2** showed the appearance of new bands characteristic of the *N*-heterocyclic carbene in the aromatic region around 140 ppm and to a lower extent in the aliphatic region at 22 ppm (ArCH₃) and at 50 ppm in **C2** (NCH₂CH₂N)



Fig. 6. Solid-state ¹³C CP-MAS NMR spectrum of hybrid material M2.



Fig. 7. DRIFT spectra of hybrid material **M1** (blue) and supported catalyst **C1** (red) wavenumber (cm⁻¹). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)



Fig. 8. Solid-state ¹³C CP-MAS NMR spectra of M1 (a) and C1 (b). *New signals.

(Figs. 8 and 9). The ¹³C CP-MAS NMR of **C2** revealed the formation of the desired complex but the weak intensity of the new signal suggested a low amount of anchored catalyst. As expected, this technique appeared much more powerful than micro-analysis by SEM-EDX to evidence slight modifications. For both catalysts **C1** and **C2**, the characteristic carbene carbons Ru=C and Ru–C(N∩N) could not be observed but it must be mentioned that these signals are sometimes difficult to observe even by NMR in solution.

Quantitative analyses were performed by ICP-OES in order to determine the ruthenium loadings. As suspected from the



Fig. 9. Solid-state ¹³C CP-MAS NMR spectra of M2 (a) and C2 (b). *New signals.



Scheme 3. Preparation of hybrid catalysts C1 and C2 (Mes = 2,4,6-trimethylphenyl, Cy = cyclohexyl).

Table 2	
Ruthenium loadings determined by ICP-OES.	

Material	wt% Ru	$\operatorname{Ru}(\operatorname{mmol} g^{-1})$	$Ru (mol m^{-2})$
C1	0.409	0.041	8.24×10^{-8}
(2	0.209	0.021	3.23×10^{-7}

qualitative analysis, the ruthenium content was higher in **M1** than in **M2** (Table 2). This difference may arise from several parameters in particular the specific surface area and porous volume of the two inorganic supports. As depicted in Table 3, the specific surface area and pore volumes determined by low temperature nitrogen adsorption experiments revealed a large difference between the two solids that certainly accounts for the results obtained. In addition, the number of accessible surface hydroxyl groups per unit area is another parameter to consider but that is difficult to evaluate. It would also be interesting to achieve an in-depth study on the role of acidity of the hydroxyl groups of the inorganic support on its ability to be more or less grafted.

In conclusion, both qualitative and quantitative analyses demonstrated the synthesis of the two supported catalysts. These two catalysts were then evaluated in catalytic metathesis reactions and the possibility to reuse these supported catalysts over several runs was also screened.

2.3. Catalytic activity and reusing of the supported catalysts

The new hybrid Hoveyda catalysts C1 and C2 grafted on silica and zirconia showed good stability upon storing at 4 °C under argon over one month without any sign of decomposition. They were engaged in a series of model ring closing metathesis reactions of N,N-diallyltosyl amide (DATA) in DMC to evaluate their activity and multiple-use (Scheme 4). For long, Hoveyda based catalysts were thought to be recyclable owing to the possibility of recovering the pre-catalyst via boomerang or return and release process. With the recent results disclosed by Plenio [25] it is more likely that only a little fraction of the pre-catalyst is initially activated leaving the remaining stable pre-catalyst available for the next run. In fact the initial pre-catalyst loading constitutes a reservoir of catalyst that is partially used in each consecutive run. In that case catalyst immobilization still presents the interest of more efficient utilisation of expensive catalysts over multiple consecutive uses by increasing Turn Over Numbers with the same initial loading.

Table 3 Specific surfac	e area and porosity of the virgin silica	and zirconia.
Matorial	Specific surface area $(m^2 g^{-1})$	Porous volumo (cm ³ g ⁻¹

Material	Specific surface area (m ² g ⁻¹)	Porous volume (cm ³ g ⁻¹)		
Silica	496	0.71		
Zirconia	64	0.21		



Scheme 4. Model RCM reaction of diallyltosyl amide.

The same protocol was used for the two supported catalysts, except the supported catalyst initial mass (55 mg of supported catalyst C1, and 106 mg of supported catalyst C2). A single load of supported catalyst corresponding to a substrate to Ru ratio of 0.7 mol% was used as well as the corresponding m_0 mass of DATA. The DATA conversion at 30 °C was monitored by gas chromatography until stable conversion was reached. The supported catalyst was then separated by mean of classical filtration and the following cycle was initiated by addition of a new load of DATA (m_0) and so on. The catalytic activity of the supported catalysts was monitored according to two criteria: the final conversion and the time to reach this conversion. As depicted in Table 4, the reaction time necessary to reach high conversion in the first run depended on the catalyst, and for a given one it was sometimes necessary to increase the reaction time in order to maintain high conversions during the following cycles.

Good conversions were obtained in short reaction times (1-5 h) with a low catalyst loading of 0.7 mol% of ruthenium in anhydrous DMC (0.05 M) at 30 °C (Table 4). The best results were obtained with the hybrid catalyst **C1** that allowed two runs with almost full conversion in a reasonable amount of time and two extra runs with good conversions. The supported catalyst **C2** also performed well in the first 2 runs but longer reaction times were required. The better results obtained with **C1** may be attributed to the better

Table 4	
Catalytic activity and multiple-use of supported catalysts C1 and C2 at 30 °C.	

Cycle	C1		C2		
	Conv. (%)	t(min)	Conv. (%)	t(min)	
1	98	105	97	211	
2	98	181	88	240	
3	81	239	54	392	
4	70	300			
5	43	300			

diffusion of reagents through the pore channels to the catalytic sites. The decrease in activity of the hybrid catalysts **C1** and **C2** during consecutive runs may have different origins such as the intrinsic stability of the catalyst (interactions with hydroxide OH), and the leaching of catalyst over time. To enhance the stability and the reuse of the hybrid catalyst, capping of free Si–OH or Zr–OH on solid supports may be envisaged as already reported [13d]. Catalyst leaching is also an important issue due to the release of the ligand on the pre-catalyst and consecutive natural deactivation. In such a case, catalyst immobilization via the NHC ligand would be a better solution to prevent ruthenium leaching [13e,g].

3. Conclusion

This study has shown the feasibility of the immobilization and multiple-use of new hybrid organic-inorganic Hoveyda catalysts in dimethyl carbonate (DMC) an eco-friendly solvent. The design, the preparation and the characterization of Hoveydatype catalysts supported onto silica (**C1**) and an original catalyst supported onto zirconia (C2) have been realised. The hybrid Hoveyda catalysts exhibited stability, activity, selectivity in a model RCM reaction and it was possible to use the catalyst over several consecutive runs. The activities of the hybrid catalysts were highly dependent on the intrinsic properties of the solid supports. To enhance the stability and reuse of the hybrid catalyst, protection of the free hydroxy groups on the solid supports may be a valuable alternative. This grafting on zirconia powder was then successfully transposed to the grafting of the zirconia active layer of a tubular inorganic ultrafiltration membrane to prepare a catalytic membrane allowing both the catalytic reaction and the separation in a single step process [32].

4. Experimental

General: All reactions were carried out under an inert atmosphere of dry argon, with standard Schlenk tube techniques. DMF was freshly distilled over CaH₂ before use. Dimethyl carbonate was distilled and stored over 4 Å molecular sieves prior to use. The second generation Grubbs catalyst was purchased from Sigma-Aldrich and stored under argon. Silica gel (Geduran Si60) was purchased from Merck. Zirconia powder was kindly provided by Orelis in 1995. Liquid NMR data were recorded on Bruker DPX 200 and Bruker Ascend 400 MHz spectrometers. The ²⁹Si and ³¹C solid state CP-MAS NMR spectra were recorded on a Bruker Avance 300 spectrometer. The recycle time were respectively 3.5 and 2 s. The rotor spinning rate was 8 kHz for ²⁹Si and 10 kHz for ¹³C. The content of ruthenium was determined at the UMR-CNRS "Sciences Chimiques de Rennes" of the University of Rennes 1 by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis. Surface areas were determined by Brunauer-Emmett-Teller (BET) method on Micromeritics ASAP 2010 analyser at the UMR-CNRS "Sciences Chimiques de Rennes" of the University of Rennes 1, and the average pore volume was calculated by the BJH method. DRIFT spectra were registered on Perkin Elmer spectrometer (Paragon 1000) using the Spectrum for windows software. Background was registered on KBr (IR grade) powder carefully grinded in an agate mortar. Supported catalysts were dispersed in KBr and carefully grinded before spectrum recording. Conditions were: average of 20 scans, resolution: 2 cm^{-1} , recording between 4000 and 600 cm⁻¹. No corrections were achieved on raw spectra that are given as registered.

4.1. Ligand synthesis

4.1.1. 3-Formyl-4-hydroxyphenyl benzoate (2)

2,5-Dihydroxybenzaldehyde (2g, 14.5 mmol, 1.0 equiv.) was dissolved in 15 mL of dry CH₂Cl₂ in a Schlenk tube. Dry Et₃N (4.4 mL, 31.9 mmol, 2.2 equiv.) was then added followed by benzoic anhydride (6.9 g, 31.9 mmol, 2.1 equiv.) and 4-dimethylaminopyridine (0.18 g, 1.4 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature for 5 h and then diluted with 40 mL of diethyl ether and washed, sequentially, with a saturated solution of NaHCO₃ and brine. The organic phase was dried over Na₂SO₄ and then concentrated under reduced pressure. The light brown residue was dissolved in a mixture of MeOH:THF (32 mL/8 mL) before addition of anhydrous K₂CO₃ (2g, 1 equiv.). The resulting mixture was stirred for 1 h and then diluted with 40 mL of diethyl ether and acidified by a dropwise addition of 20 mL of 2 N aqueous HCl. The organic phase was washed several times with a saturated solution of Na₂HPO₄ until full removal of benzoic acid (monitored by TLC). 2 was obtained as a white solid (3.3 g, 91%) of good enough purity and used without any further purification. NMR data were consistent with reported data [27]. ¹H NMR (400.16 MHz, CDCl₃, 25 °C, TMS, δ (ppm)): 7.05 (d, 2.9 Hz, 1H, CH), 7.35 (dd, 9.1 Hz, 2.9 Hz, 1H, CH), 7.42 (d, 3.0 Hz, 1H, CH), 7.55 (m, 2H), 7.69 (m, 1H), 8.25 (d, 7.9 Hz, 2H, CH), 8.89 (s, 1H, OH), 10.98 (s, 1H, CHO); 13 C NMR (50.33 MHz, CDCl₃, δ (ppm)): 114.6, 120.2, 128.2, 128.4, 132.3, 132.1, 135.1, 145.1, 159.5, 167.1, 188.2.

4.1.2. 3-Formyl-4-(propan-2-yloxy)phenyl benzoate (3)

In a Schlenk tube maintained under an argon atmosphere, **2** (1.0 g, 4.12 mmol, 1 equiv.) and K₂CO₃ (0.85 g, 6.20 mmol, 1.5 equiv.) were dissolved in dry DMF (15 mL), and were stirred for 1 h at 40 °C. 2-Bromopropane (0.58 mL, 6.20 mmol, 1.5 equiv.) dissolved in DMF (5 mL) was then added to the stirring solution. The reaction mixture was stirred overnight at 40 °C. The organic products were extracted with diethyl ether, and the resulting organic phase was washed with water. Purification by column chromatography on silica gel using petroleum ether/diethyl ether (95/5, v/v)as the eluent afforded **3** as a white solid (0.92 g, 79%). ¹H NMR (400.16 MHz, CDCl₃, 25 °C, TMS, δ (ppm)): 1.45 (d, 6.0 Hz, 6H, CH₃); 4.68 (sept, 6.0 Hz, 1H, CH), 7.05 (d, 8.8 Hz, 1H, CH), 7.21 (d, 2.3 Hz, 1H, CH), 7.40 (dd, 9.2 Hz, 2.8 Hz, 1H, CH), 7.50-7.53 (m, 2H, CH), 7.62-7.66 (m, 2H, CH), 8.18 (d, 8.0 Hz, 2H, CH), 10.51 (s, 1H, CHO). ¹³C NMR (50.33 MHz, CDCl₃, δ (ppm)): 22.4, 72.2, 115.5, 121.3, 129.1, 129.5, 130.6, 131.3, 134.2, 144.6, 158.7, 165.7, 189.6, 196.3; HRMS (EI): m/z: 284.1069 [M+.]; elemental analysis (%) calculated for C₁₇H₁₆O₄: C 71.82, H 5.67; found: C 70.93, H 5.62.

4.1.3. 3-Ethenyl-4-(propan-2-yloxy)phenyl benzoate (4)

Ph₃P⁺CH₃I⁻ (2.13 g, 5.27 mmol, 1.5 equiv.) was slowly added at room temperature to a suspension of NaH (126.6 mg, 5.27 mmol, 1.5 equiv.) in THF (15 mL), and the reaction mixture was heated at 60 °C for 2 h. After cooling to room temperature, the resulting solution was added to 3 (1.0 g, 3.51 mmol, 1 equiv.) dissolved in diethyl ether (15 mL). After stirring overnight at 30°C, the reaction was quenched by the addition of 9 mL of water and the organic products were extracted with 20 mL of diethyl ether. Purification by column chromatography on silica gel using petroleum ether/diethyl ether (95/5, v/v) as the eluent afforded **4** as a colourless solid (0.70 g)71%). ¹H NMR (400.16 MHz, CDCl₃, 25 °C, TMS, δ (ppm)): 1.36 (d, 6.0 Hz, 6H, CH₃); 4.52 (sept, 6.0 Hz, 1H, CH); 5.27 (d, 11.2 Hz, 1H, CH), 5.72 (d, 17.7 Hz, 1H, CH), 6.91 (d, 8.8 Hz, 1H), 7.01-7.09 (m, 2H, CH); 7.31 (d, 2.5 Hz, 1H, CH); 7.49-7.51 (m, 2H, CH), 7.61-7.65 (m, 1H, CH), 8.21 (d, 7.90 Hz, 2H, CH). 13 C NMR (50.33 MHz, CDCl₃, δ (ppm)): 22.6, 72.0, 115.3, 115.5, 119.7, 121.9, 129.0, 129.5, 130.1, 130.6, 131.7, 133.9, 144.9, 153.3, 165.8; HRMS (EI): m/z: 282.1232 [M⁺•].

4.1.4. 3-Ethenyl-4-(propan-2-yloxy)phenol (5)

In a Schlenk tube maintained under an argon atmosphere, 4 (1.0 g, 3.39 mmol, 1 equiv.) was dissolved in anhydrous THF (8 mL), and the reaction mixture was cooled at -45°C. Sodium methoxide (26% in MeOH, 0.71 mL, 3.39 mmol, 1 equiv.) was then added to the stirring solution, and the reaction mixture was stirred for 30 min at $-45 \,^{\circ}\text{C}$. The reaction was guenched by addition of $3 \,\text{mL}$ of a 1 N HCl solution and extracted with diethyl ether. The combined organic extracts were dried with MgSO₄, concentrated under vacuum. Purification by flash column chromatography on silica gel using PE/Et₂O (90:10, v/v) as the eluent afforded **5** as a thick oil (0.53 g, 88%). NMR data were consistent with reported data [6c]. ¹H NMR (400.16 MHz, CDCl₃, 25 °C, TMS, δ (ppm)): 1.31 (d, 6.1 Hz, 6H, CH₃); 4.35 (sept, 6.1 Hz, 1H, CH); 4.56 (bs, 1H, OH), 5.23 (d, 11.2 Hz, 1H, CH); 5.67(d, 17.6 Hz, 1H, CH); 6.68 (dd, 8.7 Hz, 2.9 Hz, 1H, CH); 6.78 (d, 8.8 Hz, 1H, CH); 6.95 (d, 2.8 Hz, 1H, CH); 7.01 (dd, 17.6 Hz, 11.2 Hz, 1H, CH).

4.1.5. 2-Ethenyl-1-(propan-2-yloxy)-4-((3-trimethoxysilyl)propyl)benzene

(6)

In a Schlenk tube maintained under an argon atmosphere, product **5** (0.2 g, 1.77 mmol, 1.5 equiv.) was slowly added at 0 °C to a suspension of NaH (42.5 mg, 1.77 mmol, 0.9 equiv.) in DMF (4 mL), and the reaction mixture was stirred at room temperature for 1 h. After cooling the reaction mixture to 0 °C, (3-iodopropyl) trimethoxysilane was added and the reaction mixture was stirred at room temperature for 1 h. After colucts were extracted with diethyl ether. The organic phase was dried with MgSO₄, filtered over a pad as silica gel and concentrated under vacuum. ¹H NMR (200.12 MHz, CDCl₃, 25 °C, TMS, δ (ppm)): 0.85 (t, 8.1 Hz, 2H, CH₂); 1.31 (d, 6.0 Hz, 6H, CH₃); 1.92 (m, 2H, CH₂); 3.65 (s, 9H, CH₃); 3.90 (m, 2H, CH₂); 4.40 (sept, 6.05 Hz, 1H, CH); 5.20 (d, 10.1 Hz, 1H, CH); 5.71 (d, 17.3 Hz, 1H, CH); 6.71–6.85 (m, 2H, CH); 6.90–7.15 (m, 2H, CH); HRMS (ESI): m/z: 363.1605 [M+Na]⁺ calculated for C₁₇H₂₈O₅NaSi: 363.16037.

4.1.6. Synthesis of the hybrid silica material (M1)

In a Schlenk tube maintained under an argon atmosphere, silica gel (Merck) (1.1 g, 18 mmol) dried for 24 h at 70 °C under vacuum was added at room temperature to a solution of ligand **6** (0.3 g, 0.88 mmol) in dry toluene (15 mL). The reaction mixture was refluxed for 24 h. After cooling the reaction mixture at room temperature, the silica gel was washed successively four times with CH₂Cl₂, diethyl ether and then with pentane. The solid was dried under vacuum overnight affording **M1** as a white powder. ²⁹Si CP-MAS NMR: δ (ppm): -58 (T²), -66 (T³), -90 (Q²), -101 (Q³), -110 (Q⁴); ³¹C CP-MAS NMR: δ (ppm): 6 (CH₂), 20 (CH₃), 49 (O-CH₃), 73 (CH, CH₂), 110–119 (CH₃ aromatic, CH₂ styrene), 126 (C aromatic, CH styrene), 135 (C aromatic), 137 (C aromatic). DRIFT: (KBr): ν (cm⁻¹): 2974: ν (CH₃, CH₂) symmetric, 2937: ν (CH₃, CH₂) asymmetric, 1652: ν (C=C) styrene, 1452: ν (C=C) aromatic, 1387: δ (CH₃), 1312: δ (CH₂).

4.1.7. Synthesis of the hybrid zirconia material (M2)

In a Schlenk tube maintained under an argon atmosphere, zirconia (351 mg, 2.85 mmol) pre-treated at 70 °C for 24 h was added at room temperature to a solution of ligand **6** (0.26 g, 0.75 mmol) dissolved in dry toluene (15 mL). The reaction mixture was refluxed for 24 h. After cooling the reaction mixture at room temperature, the zirconia was washed successively four times with CH₂Cl₂, diethyl ether and then with pentane. The solid was dried under vacuum overnight affording **M2** as a white powder. ²⁹Si CP-MAS NMR: δ (ppm): large signal (-55 to -45); 31 C CP-MAS NMR: δ (ppm): 7 (CH₂), 20 (2CH₃), 49 (O–CH₃), 73 (CH, CH₂), 110–119 (3CH₃ aromatic, CH₂ styrene), 126 (C aromatic, CH styrene), 135 (C aromatic), 137 (C aromatic).

DRIFT: (KBr): ν (cm⁻¹): 2974: ν (CH₃, CH₂) symmetric, 2937: ν (CH₃, CH₂) asymmetric, 1652: ν (C=C) styrene, 1452: ν (C=C) aromatic, 1387: δ (CH₃), 1312: δ (CH₂).

4.1.8. Synthesis of the hybrid silica catalyst (C1)

In a Schlenk tube maintained under an argon atmosphere, Grubbs second generation catalyst (9.2 mg, 0.011 mmol) was added to a solution of hybrid material **M1** (202 mg) in anhydrous and degassed CH₂Cl₂ (15 mL). The reaction mixture was refluxed at 40 °C for 12 h. After cooling the reaction mixture at room temperature, the silica gel was washed successively with CH₂Cl₂ until the filtrate had no colour, and dried under vacuum overnight to obtain as a green powder. ²⁹Si CP-MAS NMR: δ (ppm): -58 (T²), -66 (T³), -90 (Q²), -101 (Q³), -110 (Q⁴). ³¹C CP-MAS NMR: δ (ppm): 6 (CH₂), 20 (CH₃), 22 (CH₃), 49 (O–CH₃), 73 (CH, CH₂), 110–119 (CH₃ aromatic, CH₂ styrene), 126 (C aromatic, CH styrene), 129 (CH aromatic) 135 (C aromatic), 137 (C aromatic). ICP-OES: Ru: 0.041 mmol Ru/g of silica, 4.0×10^{-3} mole of catalyst/100 mg of silica SiO₂ grafted $\rightarrow 8.24 \times 10^{-8}$ mol m⁻².

4.1.9. Synthesis of the hybrid zirconia catalyst (C2)

In a Schlenk tube maintained under an argon atmosphere, Grubbs second generation catalysts (20.9 mg, 0.025 mmol) was added to a solution of hybrid material **M2** (293 mg) in anhydrous and degassed CH₂Cl₂ (15 mL). The reaction mixture was refluxed for 12 h. After cooling the reaction mixture at room temperature, the silica gel was washed successively with CH₂Cl₂ until the filtrate had no colour, and dried under vacuum overnight to obtain as a green powder. ²⁹Si CP-MAS NMR: δ (ppm): large signal (–55 to –45). ³¹C CP-MAS NMR: δ (ppm): 6 (CH₂), 20 (CH₃), 22 (CH₃), 49 (O–CH₃), 73 (CH, CH₂), 110–119 (CH₃ aromatic, CH₂ styrene), 126 (C aromatic), 137 (C aromatic). ICP-OES: Ru: 2.07 × 10⁻³ mole of catalyst/100 mg of zirconia grafted \rightarrow 3.23 × 10⁻⁷ mol m⁻².

4.1.10. Typical procedure for RCM reactions of DATA and multiple-use

A solution of diallytosylamide DATA (80 mg, 0.32 mmol) in anhydrous DMC (4 mL) was added under nitrogen to catalyst **C1** or **C2** (0.7 mol% Ru) and the mixture was stirred under argon at $30 \degree$ C. Reaction samples were analysed by gas chromatography at regular intervals. The reaction mixture was cannula filtered under nitrogen atmosphere and the solid was washed four times with 4 mL of anhydrous DMC. A new run was started by addition of 4 mL of anhydrous DMC and DATA (80 mg, 0.32 mmol) to the solid catalyst **C1** or **C2**.

4.1.11. Conversion of DATA by metathesis monitored by GC analysis

Conversion of diallytosylamide (DATA) was determined by gas chromatography quantification using a mainly apolar stationary phase made of PDMS-PDPS (95-5) in a semicapillary column (EquityTM-5, 30 m × 0.53 mm × 1.5 μ m film thickness, provided by Supelco). Injection at 250 °C was followed by analysis at a constant temperature of 230 °C, and the detection was obtained by a FID detector at 250 °C. The carrier gas was nitrogen at 18 kPa. The RSD value on the concentration of DATA was less than 1%, thus the accuracy on conversion was better than 2%.

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