A new heterogeneous hybrid ruthenium catalyst being an eco-friendly option for the production of polymers and organic intermediates

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We succeeded in synthesising and characterising a new heterogeneous hybrid ruthenium catalyst that exhibits excellent stability, reusability and leaching characteristics. The host–guest interaction is studied by XRD, XRF, ICP/MS, BET, FT-Raman and solid state NMR analysis. Moreover, we tested this catalytic system in ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), Kharasch addition, atom transfer radical polymerization (ATRP) and vinylation reactions. The results obtained from these tests show that for ROMP, RCM, Kharasch addition and vinylation reactions the heterogeneous catalyst possesses important advantages in comparison with its homogeneous analogue.

1. Introduction

Awareness of environmental issues has proven to be a potent driving force in the development of environment friendly processes and technologies in the chemical industry.[1] This has manifested in a determined effort, on the part of the industry, to develop catalytic processes which obviate waste production, *i.e.* solving the problem at the beginning and not dealing with the waste disposal later.[2] As a consequence of the inherent advantages of heterogeneous reagents, much effort has been directed towards the development of heterogeneous processes and the heterogenization of known active homogeneous catalysts.[3] One of the major goals of green chemistry is to develop environmentally acceptable routes to important organic products. Methods by which this can be achieved are increasing product selectivity, aiming for 100% atom efficiency and replacing stoichiometric reagents with heterogeneous catalysts. Increasingly tighter guidelines are being issued concerning the disposal of waste materials, with increasing public and corporate pressure to comply with them. In this respect it was our goal to apply the principles of making chemistry more environmentally friendly, being applied to the homogeneous catalyst **1** (Fig. 1) for which the synthesis and activity in Ring Closing Metathesis (RCM), Ring Opening Metathesis Polymerization (ROMP), Atom Transfer Radical Polymerization (ATRP), Kharasch addition and vinylation reactions, were recently reported by us.[4]

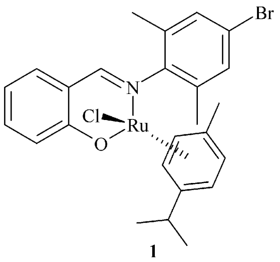

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Fig. 1 Homogeneous catalyst **1**.

Olefin metathesis is a catalytic reaction in which alkenes are converted into new products *via* the rupture and reformation of C–C double bonds. Depending on the starting material (cyclic or acyclic alkenes) and the reaction parameters, RCM, acyclic diene metathesis (ADMET) or ROMP proceed (Scheme 1, A).[5]

ATRP is based on a dynamic equilibration between the propagating radicals and the dormant species which is established through the reversible transition metal-catalysed cleavage of the covalent carbon–halogen bond in the dormant species (Scheme 1, B).[6]

The Kharasch reaction consists of the addition of a polyhalogenated alkane across an olefin through a radical mechanism (Scheme 1, C).[7]

In the enol ester synthesis the ruthenium(II) complexes promote the electrophilic activation of alkynes to give Markovnikov or anti-Markovnikov (*E* and *Z*) addition reactions of carboxylic acids to the triple bond (Scheme 1, D).[8]

Besides the formation of the (*E*)-alk-1-enyl ester, also a small percentage of (*Z*)-alk-1-enyl ester, Markovnikov addition products and disubstituted enol esters are obtained.

It is known from the literature that a limitation of ruthenium(II) complexes containing an electron-donating bidentate nitrogen ligand is the ability of these complexes to dimerize terminal alkynes into enynes (Scheme 1, E).[9]

The use of a reaction system in which the catalyst is in a different phase to that of the substrate and the products allows easy removal of the catalyst from the reaction mixture *via* filtration, centrifugation or decantation. The potential technological advantages in converting a process catalysed by a homogeneous metal complex into one involving a heterogeneous analogue have been well rehearsed.[10] Suffice to say that on a laboratory scale supported metal complex catalysts considerably facilitate product work-up and isolation, while on a large scale such heterogeneous species allow processes to be run continuously using packed or fluidised bed columns with considerable financial advantages both in terms of capital expenditure on plant and with regard to recurrent costs.

A heterogeneous catalytically active material can be formed by immobilising active species on or in a support material such

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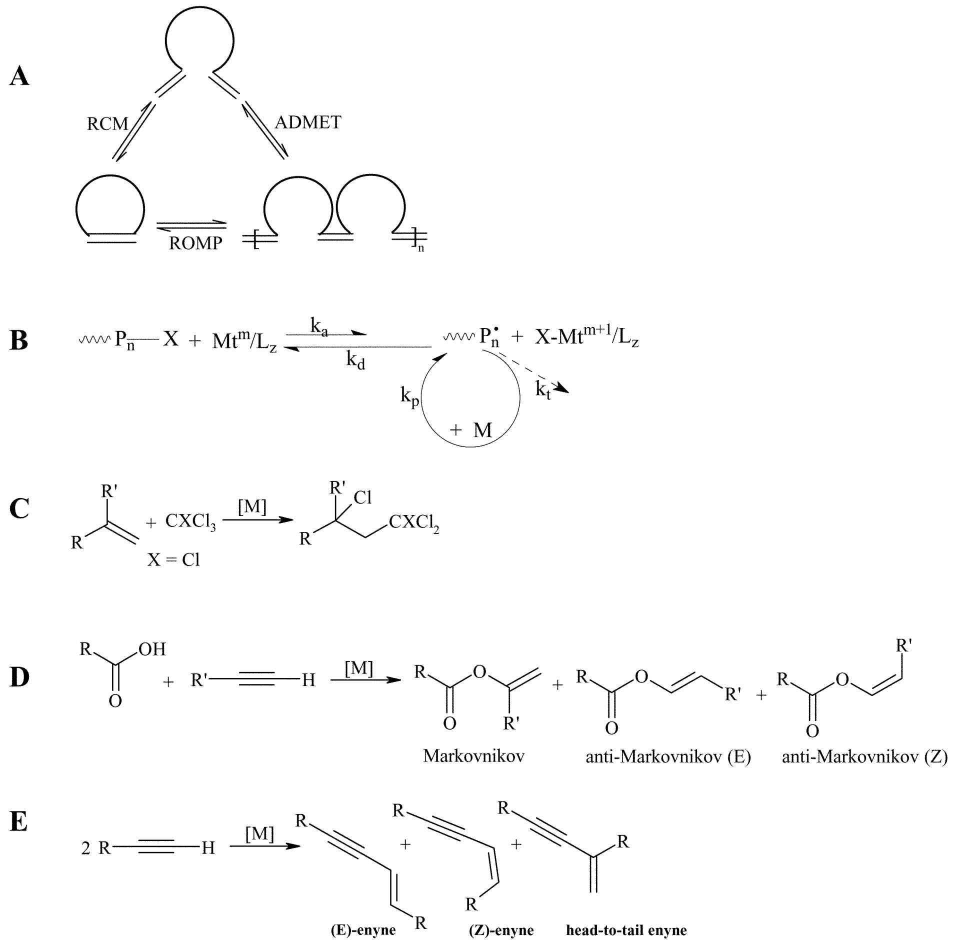


Scheme 1 Schematic representation of olefin metathesis (A), ATRP (B), Kharasch addition (C), vinylation (D) and dimerization (E).

as porous silica, titania or alumina.[11] The porosity of such materials can lead to increased reaction selectivity by giving high selectivity to the desired product. This is the ideal situation and can be achieved by the synthesis of chemically modified porous solids or supported reagent catalysts.[12] The present paper reports on the application of hybrid heterogeneous catalyst **2** (Fig. 2) prepared by the covalent anchoring of catalytic complex **1** *via* a spacer molecule onto mesoporous silica.

Furthermore, the activity of this new material was compared to that of the homogeneous analogue.

2. Experimental

2.1. General

All reactions and manipulations were performed under an argon atmosphere by using conventional Schlenk-tube techniques. Argon gas was dried by passage through P_2O_5 (Aldrich 97%). ^{1}H-NMR spectra (500 MHz) were recorded on a Bruker AM spectrometer. The chemical shifts are reported in ppm and TMS was used as reference compound. Solid-state NMR spectra were acquired on a Bruker DSX-300 spectrometer operating at 300.18 MHz for ^{1}H-NMR, 75.49 MHz for ^{13}C-NMR, 121.51 MHz for ^{31}P-NMR and 59.595 MHz for ^{29}Si-NMR. The spectra were recorded under MAS conditions with a classical 4 mm probe head allowing spinning frequencies up to 12 kHz. The anchoring of the homogeneous catalyst was confirmed by a Raman spectrometer Bruker Equinox 55 with a FRA 106 module. The loading of the heterogeneous hybrid catalyst was determined with a Varian Liberty ICP/MS spectrometer and an ARL 9400 Sequential XRF spectrometer. XRD spectra were recorded on a Siemens diffractometer D5000. Elemental analyses were performed with Carlo Erba EA 1110 equipment. The BET analysis was done on a Gemini Micromeritics 2360 surface area analyser with Flow prep 060 degasser. The samples were dried overnight at 423 K and cooled to room temperature prior to adsorption. Extra care with the functionalised materials was necessary due to the possibility of aerial oxidation, therefore transfer to the balance and outgassing of the system was fast. Nitrogen isotherms were recorded at 77 K. Specific surface areas were determined from the linear part of the BET plot ($P/P_0 = 0.05$–0.3). The number- and weight-average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) of the polymers were determined by gel permeation chromatography (CHCl$_3$, 25 °C) using polystyrene (for styrene) or polyMMA (for the acrylates and methacrylates) standards. The GPC instrument used was a Waters Maxima 820 system equipped with a PL gel column. For ATRP and Kharasch addition reactions, all reagents and solvents were dried, distilled and stored under nitrogen at −20 °C with conventional methods. ATRP of methacrylates [methyl methacrylate (MMA), isobutyl methacrylate (IBMA)],

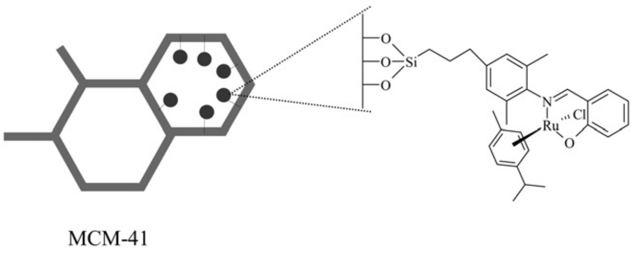


Fig. 2 Cartoon type representation of the hybrid catalytic system **4**.

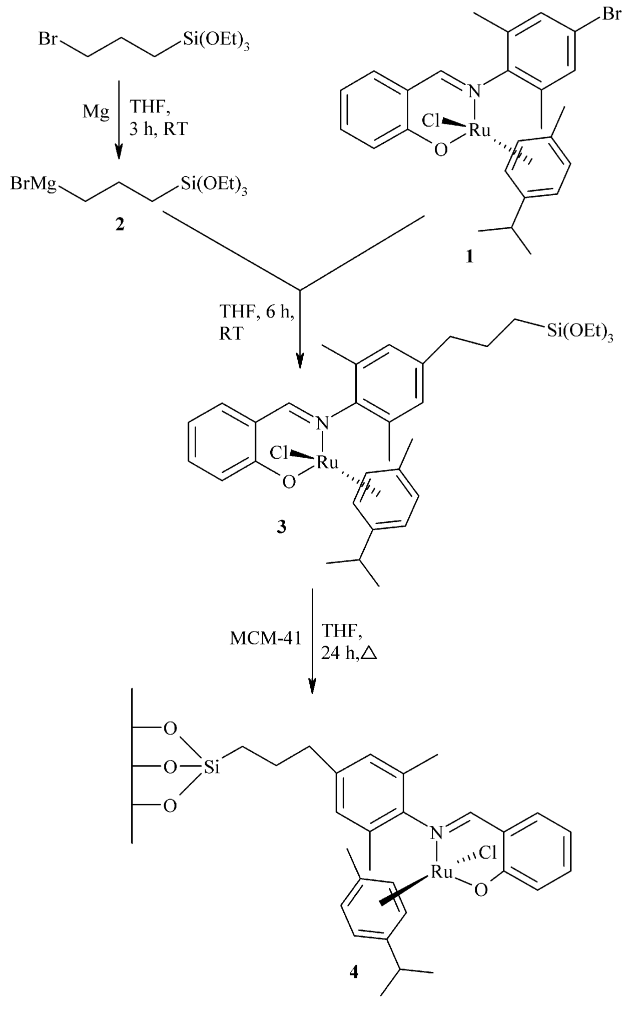
acrylates [methyl acrylate (MA), butyl acrylate (BA)] and styrene (Styr) was carried out with respectively ethyl 2-methyl-2-bromopropionate, methyl 2-bromopropionate and (1-bromoethyl)benzene as initiator. GC analysis was performed using the following conditions: column: SPB®-5; 30 m × 0.25 mm × 0.25 µm film thickness; carrier gas: He, 100 kPa; detector: FID; gas chromatograph: Varian 3300; integrator: Vista 401. GC/MS measurements were performed using the following conditions: column: SPB®-5; 30 m × 0.25 mm × 0.25 µm film thickness; carrier gas: He, 100 kPa; detector: FID; gas chromatograph: Varian 4600; MS: Finnigan MAT ITD. The homogeneous catalyst was prepared according to literature procedures.[4] Cyclooctene and norbornene were purchased from Aldrich and distilled from CaH_2 under nitrogen prior to use. Commercial grade solvents were dried and deoxygenated for at least 24 h over appropriate drying agents under nitrogen atmosphere distilled prior to use. Unless otherwise noted, all other compounds were purchased from Aldrich Chemical Co., and used as received.

2.2. MCM-41

MCM-41 was synthesised as described previously.[13] After calcination the mesoporous material was characterised by XRD, N_2 adsorption and Raman spectroscopy. MCM-41 is dried overnight *in vacuo* at 423 K to achieve complete thermodesorption of physically adsorbed water from the silica surface.

2.3. Synthesis of the heterogeneous catalyst 4 (Scheme 2)

Synthesis of the organomagnesium compound 2. To a suspension of 2 mmol Mg powder in THF (10 ml), a solution of 2 mmol of bromopropyltriethoxysilane in 1 ml THF was added dropwise. Thereafter the reaction mixture was stirred for 3 h at RT.



Scheme 2 Synthesis of the heterogeneous catalyst **4**.

Synthesis of 3. The organomagnesium derivative **2** was transferred quantitatively to a solution of 2 mmol of **1** in THF (15 ml) and stirred for 6 h at RT to afford the spacer-modified catalyst **3**. The $MgBr_2$ (by-product of the reaction) was filtered off under nitrogen atmosphere. After evaporation of the solvent, **3** appeared as a brown solid. ^{1}H-NMR ($CDCl_3$) δ 8.22 (s, 1H), 7.24 (s, 2H), 6.98–6.81 (m, 4H), 5.47 (d, 2H), 5.34 (d, 2H), 3.81 (q, 6H), 2.81 (sp, 1H), 2.48 (s, 6H), 2.19 (s, 3H), 1.65 (t, 2H), 1.29 (m, 4H), 1.24 (d, 6H), 1.18 (t, 9H); elemental analysis calcd. (%) for $RuC_{34}H_{48}O_4NClSi$ (699.29): C 58.39, H 6.92, N 2.00; found: C 58.28, H 6.87, N 2.07%.

Anchoring of 3 on MCM-41. 2 mmol of **3** was dissolved in 15 ml THF. This solution was quantitatively transferred to 2 g MCM-41 that was dried overnight at 150 °C under vacuum. After 24 h stirring at RT the heterogeneous catalyst **4** was filtered off under nitrogen atmosphere and washed with cold THF (5 × 15 ml). ICP-MS measurements reveal that the Ru amount in the washing phase (unreacted part of the initial 2 mmol) is compatible with the 0.89 wt% found for **4**.

2.4. ROMP experiments

In a typical ROMP experiment 0.005 mmol of the catalyst suspension in toluene was transferred into a 15 ml vessel followed by the addition of a catalytic amount (2 equiv.) of trimethylsilyldiazomethane (TMSD) diluted in 1 ml toluene *via* a precision syringe over 0.5 h to allow the formation of the initiating metal carbene species. Then the monomer solution in toluene (800 equivalents for norbornene, 200 equivalents for cyclooctene) was added and the reaction mixture was kept stirring at 85 °C for 3 hours. To stop the polymerization reaction, 2–3 ml of an ethyl vinyl ether/2,6-di-*tert*-butyl-4-methylphenol (BHT) solution is added and the solution is stirred till the deactivation of the active species is completed. The solution is poured into 50 ml methanol (containing 0.1% BHT) and the polymers are precipitated and filtered off. To remove the remaining heterogeneous catalyst from the polymers, they are dissolved in $CHCl_3$ so that the catalyst can be filtered off. The $CHCl_3$ is then removed *in vacuo* from the polymer solution until a high viscosity is reached after which the polymers are precipitated by adding 100 ml methanol. The as-obtained white polymers are then filtered off and dried in vacuum overnight.

2.5. RCM experiments

All reactions were performed on the bench top in air by weighing 5 mol% of the catalyst into a dry 10 ml vessel and suspending the solid in 2 ml toluene. Then we added a catalytic amount (2 equiv.) of trimethylsilyldiazomethane (TMSD) diluted in 1 ml toluene *via* a precision syringe over 0.5 h to allow the formation of the initiating metal carbene species. A solution of the appropriate substrate (0.1 mmol) in toluene (2 ml) was added, together with the internal standard dodecane. The reaction mixture was stirred for 17 hours at 85 °C. Product formation (all reaction products were unambiguously identified previously[4b] and diene disappearance were monitored by GC analysis and confirmed in reproducibility experiments by ^{1}H-NMR spectroscopy through integration of the allylic methylene peaks (here the solvent was deuterated toluene and the internal standard 1,3,5-mesitylene). GC analysis of the reaction mixture also ruled out the formation of cycloisomers, oligomers or telomers.

2.6. ATRP experiments

In a typical ATRP experiment 0.0117 mmol of catalyst was placed in a glass tube (in which the air was expelled by three vacuum–nitrogen cycles) containing a magnet barr and capped by a three-way stopcock. Then the monomer and initiator were added so that the molar ratios [catalyst]/[initiator]/[monomer] were 1/2/800. All liquids were handled under argon with dried syringes. The reaction mixture was then heated for 17 h at the reaction temperature, which was 85 °C for the acrylates and methacrylates and 110 °C for styrene. After cooling, it was diluted in THF and poured in 50 ml n-heptane (for the acrylates and methacrylates) or 50 ml methanol (for styrene) under vigorous stirring after which the precipitated polymer was filtered with suction. To remove the remaining heterogeneous catalyst from the polymers, they were dissolved in $CHCl_3$ so that the catalyst could be filtered off. The $CHCl_3$ was then removed *in vacuo* from the polymer solution until a high viscosity was reached after which the polymers were precipitated by adding 100 ml n-heptane (for the acrylates and methacrylates) or 100 ml methanol (for styrene). The as-obtained white polymers were then filtered off and dried in vacuum overnight.

2.7. Kharasch addition experiments

All reactions were performed on the bench top in air by weighing 0.01 mmol of the catalyst into a dry 10 ml vessel and suspending the solid in 2 ml toluene. Then the solution of alkene (3 mmol), CCl_4 (4.33 mmol) and dodecane (0.083 ml) in toluene (1 ml) were added after which the reaction mixture was heated at 85 °C for 17 h. The yields were obtained by GC analysis of the reaction mixture using dodecane as internal standard.

2.8. Vinylation experiments

In a typical vinylation experiment, 4.4 mmol of carboxylic acid, 4.4 mmol of alkyne and 0.04 mmol of catalyst were transferred in a 15 ml glass vessel containing 3 ml toluene. Then the reaction mixture was heated for 4 hours at 100 °C under an inert atmosphere. The total yield was determined with Raman spectroscopy by following the diminishing intensity of the $\nu_{C=C}$ of phenylacetylene and octadiyne and using a calibration curve (Conformation was obtained by GC/MS). The selectivities were determined by GC/MS making use of the different fragmentations of the isomers. GC/MS measurements excluded also the formation of other products than those reported here.

3. Results and discussion

3.1. Characterisation

3.1.1. X-Ray diffraction (XRD). The XRD pattern of the pristine MCM-41 sample (Fig. 3) has a sharp d_{100} peak as well as secondary diffractions observed at larger angles (d_{110} and d_{200}), indicating the presence of hexagonally arranged pore structures, which are characteristic for MCM-41 solids. The d_{100} spacing amounts to 3.714 nm. The hexagonal unit cell parameter a_0, a measure of the spacing between the hexagonal layers, is calculated as $2d_{100}/\sqrt{3}$. This parameter is related to the average distance between pores in a two-dimensional framework, and for an ideal structure the parameter is equal to the internal pore diameter plus the thickness of the pore walls. For the pristine MCM-41 we find that $a_0 = 4.289$ nm. As the pattern of the XRD spectrum is the same for the heterogeneous catalyst and the pristine MCM-41, we can conclude that the anchoring of the catalyst *via* a spacer molecule did not affect the hexagonal long-range-ordered structure of the mesoporous MCM-41. For the heterogeneous catalyst the d_{100} spacing and a_0 amount to respectively 3.692 nm and 4.26 nm.

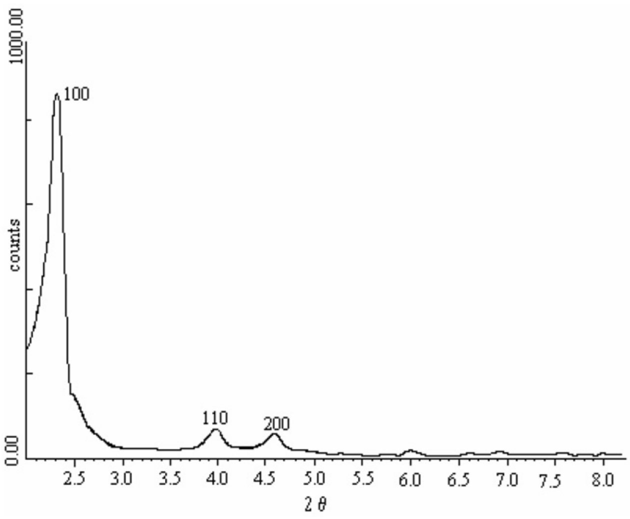


Fig. 3 XRD pattern of the pristine MCM-41.

3.1.2. N_2 adsorption analysis. The pore size distributions (PSD) of both the pristine MCM-41 and the heterogeneous catalyst were calculated using the desorption branches of the N_2 adsorption isotherms and the Barrett–Joyner–Halenda (BJH) algorithm[14] (Fig. 4).

The BJH algorithm is a classical method that treats adsorbed molecules as a separate, homogeneous, compressible phase in equilibrium with the gas phase. The method uses Harkins and Jura's thickness equation (which gives the thickness of the adsorbed layer of molecules on a flat surface at a given pressure), and the Kelvin equation to account for capillary effects in the porous solid. Since the Kelvin equation is not valid for pores below 1.8 nm, the BJH approach can only be used for mesoporous materials.

Specific surface areas were calculated using the BET (Brunauer, Emmett and Teller) equation. The BET equation was developed to estimate the specific surface area of non-porous solids.[15] Adsorption in non-porous solids can be modelled as adsorption on a flat surface. In a cylindrical mesopore of ~3.0 nm in diameter, the formation of the monolayer is only negligibly affected by the wall curvature and by the presence of the opposite wall surface. Since in the case of nitrogen adsorption within MCM-41, the size (~0.3 nm) of the adsorptive molecule is small compared with the size of the pore diameter (3.0 nm), the BET equation can be justifiably used to estimate the specific surface area of this solid.

The data obtained from the N_2 adsorption measurements and the XRD analyses are summarized in Table 1. The observed specific surface area for the pristine MCM-41 is 1303 $m^2\ g^{-1}$ and the pore volume is 1.0213 $cm^3\ g^{-1}$. The mesopore diameter of the pristine MCM-41, which has a value of 2.53 nm, was obtained from the PSD curve (Fig. 4, A). The

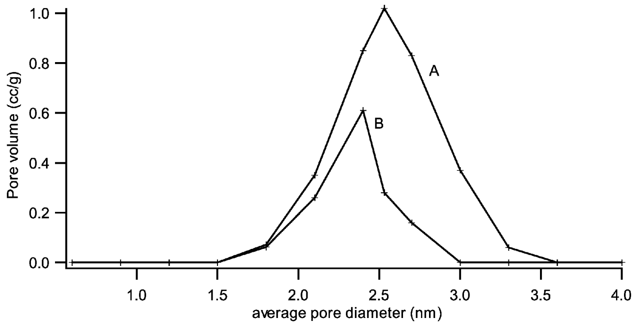


Fig. 4 Pore size distributions of both the pristine MCM-41 (A) and the heterogeneous catalyst **4** (B).

Table 1 Comparison of the properties of pristine MCM-41 and the heterogeneous catalyst **4**

	Specific surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Pore diameter/ nm	Wall thickness/ nm
MCM-41	1303	1.0213	2.53	1.76
Heterogeneous catalyst **4**	625	0.6216	2.43	1.83

wall thickness is derived from the position of the [100] peak (d_{100}) and the specific mesopore diameter. Wall thickness = $[a_0 - d_{\text{MCM-41}}]$ = 1.76 nm. The PSD of the heterogeneous catalyst (Fig. 4, B) clearly shows that the pore size of the MCM-41 is slightly decreased from 2.53 nm to 2.43 nm. Moreover we also see a reduction of the pore volume and the specific surface area (respectively from 1.0213 to 0.6216 cm^3 g^{-1} and from 1303 to 625 m^2 g^{-1}). All these results indicate that the internal pores of the MCM-41 are occupied by the catalytic complex (compound **4**, Scheme 2) and that the accessibility of the mesopores is maintained after modification.

3.1.3. Raman spectroscopy. The anchoring of the spacer modified homogeneous complex (compound **3**, Scheme 2) was also checked using Raman spectroscopy (Fig. 5).

The low intensity scattered by the mesoporous support makes it possible to examine the grafting of the homogeneous catalyst. The comparison of the Raman spectra of the pristine MCM-41 (Fig. 5, A) and the heterogeneous catalyst **4** (Fig. 5, C) clearly shows the grafting of the homogeneous species. Comparison of the Raman spectrum of the spacer modified homogeneous catalyst **3** (Fig. 5, B) and hybrid catalyst **4** (Fig. 5, C) was performed to eliminate any doubt concerning the chemical attachment of the homogeneous catalyst. We clearly see that every peak in the spectrum of the homogeneous catalyst **3** is also present in the spectrum of the heterogeneous catalyst **4**. The small shifts of some peaks in Fig. 5, C compared with Fig. 5, B indicate the change in chemical environment of the different functional groups originating from the chemical attachment of the catalyst to the carrier.

3.1.4. X-Ray fluorescence (XRF) and inductive coupled plasma/mass spectrometry (ICP/MS). XRF measurements reveal a loading of 0.088 mmol (0.89 wt% Ru) Ru complex/ g heterogeneous catalyst. This loading was confirmed by ICP/MS analysis of the heterogeneous hybrid catalyst.

3.1.5. Solid state NMR analysis. The structure of the heterogeneous catalyst **4** was also studied by solid state NMR. For the pristine MCM-41, the proton spectrum only reveals the presence of silanol groups and water. In the ^{29}Si CP MAS NMR spectrum of the pristine MCM-41 three different peaks at 90 ppm, 100 ppm and 110 ppm are observed. These values can be attributed to respectively $Si(OH)_2(OSi)_2$, $Si(OH)(OSi)_3$ and $Si(OSi)_4$. The proton spectrum of the MCM-41 + the spacer molecule (bromopropyltriethoxysilane) only reveals the presence of $-CH_2$ and $-CH_3$ groups. However, the ^{13}C CP MAS NMR spectrum of this sample reveals some interesting features. Two peaks at 50 ppm and 36 ppm can be attributed to respectively a $-OCH_2-$ and a $-CH_2Br-$ configuration. Furthermore, at 11 ppm there is an overlapping of the bands assigned to $-CH_3$ and $-SiCH_2-$ groups. The ^{29}Si CP MAS NMR spectrum of the MCM-41 + spacer reveals unambiguously the presence of a $(SiO)_3Si^*C-$ species at −58.19 ppm and a $(SiO)_2(OEt)Si^*C-$ species at −106.5 ppm. The proton spectrum of the heterogeneous hybrid catalyst only reveals the presence of aromatic and aliphatic protons as broad unresolved peaks. At 9.80 ppm a small peak of the imine proton is present. The ^{13}C CP MAS NMR spectrum of the heterogeneous catalyst reveals around 166 ppm the carbon of the $-C{=}N-$ bond. Again the aromatic and aliphatic carbon atoms can be revealed from the spectrum. Around 9.8 ppm the overlapping of the $-CH_3$ and the $-SiCH_2-$ peaks is observed again. The ^{29}Si CP MAS NMR spectrum of the heterogeneous catalyst also reveals the presence of a $(SiO)_3Si^*C-$ species at −59.69 ppm and a $(SiO)_2(OEt)Si^*C-$ species at −106.0 ppm. From all this we can conclude that the anchoring of the homogeneous catalyst *via* the spacer molecule onto the MCM-41 can take place with two or three covalent bonds. Furthermore, these results prove that it is the spacer molecule that links the catalytic metal centre to the mesoporous carrier.

3.2. Catalysis

3.2.1. Ring opening metathesis polymerization (ROMP). The results of the ROMP experiments with catalytic systems **1**^{4a} and **4** are summarized in Table 2. For details concerning the reaction conditions see the Experimental section.

From the results gathered in Table 2 it is clear that the heterogeneous catalyst **4** reaches lower yields than its homogeneous analogue **1**, and this is the case for both the strained norbornene and the less-strained cyclooctene. However, looking at the polydispersities (PDI) of the formed polymers reveals that with the heterogeneous system a much more controlled polymerization occurs (PDI 6.95 *versus* 2.34 for norbornene and 4.62 *versus* 2.95 for cyclooctene). This is an indication that only one heterogeneous catalytically active species is formed, but still diffusion limitations occur in the channels of the MCM-41. The anchoring of the homogeneous catalyst probably limits the appearance of backbiting reactions because the channels induce a certain steric hindrance which

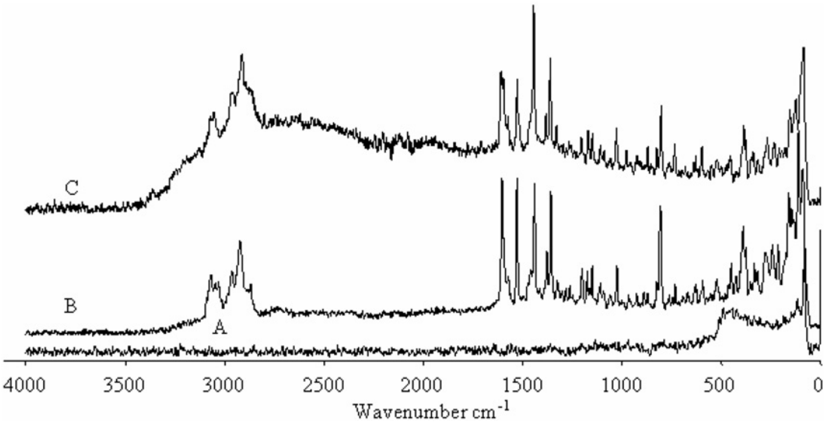


Fig. 5 Raman spectra of the pristine MCM-41 (A), the spacer modified homogeneous catalyst **3** (B) and the hybrid catalyst **4** (C).

Table 2 ROMP of norbornene and cyclooctene using catalytic systems **1** and **4**

	1/4				
	Yield (%)	M_n ($\times10^3$)	M_w ($\times10^3$)	PDI	*cis/trans*
norbornene (800 eq., 85 °C, 3 h)	98/73	98/69	682/163	6.95/2.34	0.39/0.35
cyclooctene (200 eq., 85 °C, 3 h)	71/65	57/44	262/131	4.62/2.95	0.38/0.40

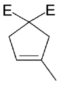
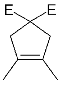
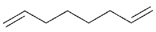
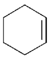
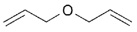
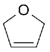
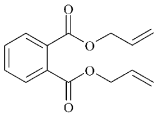
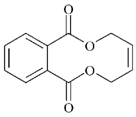
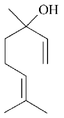
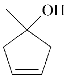
impedes the polymers from folding themselves into a position suitable to perform backbiting reactions. Also the fact that dismutation and coupling reactions are eliminated through the linking of the homogeneous species to the mesoporous carrier may be attributed to a narrowing of the PDI of the polymers formed with the heterogeneous system.

3.2.2. Ring closing metathesis (RCM).

The RCM activities of catalysts **1**[4a] and **4** are summarised in Table 3. For details concerning the reaction conditions see the Experimental section.

An important trend that can be observed from the results in Table 3 is the comparable yields of the heterogeneous and the homogeneous catalytic system. Both systems quantitatively convert diethyldiallyl malonate (entry 1), 1,7-octadiene (entry 4) and diallyl ether (entry 5). Moreover both systems also smoothly convert the tri-substituted malonate derivative (entry 2), diallylphthalate (entry 6) and linalool (entry 7). In addition, both systems succeed in yielding the ring-closed tetra-substituted malonate derivative (entry 3) in moderate yield.

Table 3 RCM of some representative substrates with catalytic systems **1** and **4** (E = COOEt)

			Isolated yield (%)	
Entry	Substrate	Product	1	4
1			100	100
2			71	73
3			23	21
4			100	100
5			100	100
6			94	89
7			76	78

3.2.3. Atom transfer radical polymerization (ATRP).

The results of the ATRP experiments using catalytic systems **1**[4a] and **4** are gathered in Table 4. For details concerning the reaction conditions see the Experimental section.

The results gathered in Table 4 show a marked decrease in % yield when the heterogeneous system is used for conducting the ATRP experiments. Moreover, the decrease in initiation efficiency and the increasing polydispersities of the formed polystyrene and polymethyl methacrylate indicate a loss of control over polymerization when the heterogeneous catalytic system **4** is used. From these results it is obvious that for ATRP reactions, the immobilisation of the homogeneous catalyst **1** on a mesoporous silica carrier *via* a spacer molecule is not advantageous for the polymer properties.

3.2.4. Kharasch addition.

In Table 5 the results of the Kharasch addition experiments of CCl_4 across some representative olefins and using catalytic systems **1**[4a] and **4** are summarised. For details concerning the reaction conditions see the Experimental section.

It is clear that for Kharasch addition reactions of CCl_4 across the olefins depicted in Table 5, the % yields obtained with the heterogeneous system **4** are slightly lower in comparison withthe homogeneous compound **1**. However, the very easy separation of the catalyst from the reaction mixture in the case of the heterogeneous compound **4** (the separation can be done by simple filtration) makes the latter system much more suitable for performing Kharasch addition reactions than its homogeneous counterpart **1**.

3.2.5. Vinylation.

In Table 6 the results of the vinylation reactions using catalytic systems **1**[4a] and **4** are summarised. For details concerning the reaction conditions see the Experimental section.

When octadiyne is used as a substrate, the addition of both carboxylic acids result in the selective formation of (*E*)-alk-1-enyl esters corresponding to a regio- and stereoselective anti-Markovnikov addition of the acid to the triple bond and this is irrespective of the catalytic system used. The percentage of (*E*)-alk-1-enyl ester is for the two catalytic systems and both acids more or less the same and varies in the range of 74%–79%. The total yield, however, is dependent on the type of catalyst and acid used. Whereas for formic acid the two catalytic compounds reach comparable total yields, for acetic acid the heterogeneous system **4** shows a somewhat higher activity.

Table 4 ATRP of some representative substrates using catalytic systems **1** and **4**

	Yield (%)	M_n ($\times10^3$)	M_w ($\times10^3$)	PDI	f_i[a]
Methyl methacrylate	84/76	48/60	84/126	1.75/2.11	0.71/0.51
Isobutyl methacrylate	62/53	—	—	—	—
Methyl acrylate	54/38	—	—	—	—
n-Butyl acrylate	35/26	—	—	—	—
Styrene	95/86	54/63	98/134	1.81/2.15	0.70/0.57

[a] f_i = Initiation efficiency = $M_{n,theor.}/M_{n,exp.}$ with $M_{n,theor.}$ = ([monomer]$_0$/[initiator]$_0$) × MW(monomer) × conversion.

Table 5 Karasch addition reaction of CCl_4 of some representative olefins using catalytic systems **1** and **4**

	Yield (%) using **1**/**4**
Methyl methacrylate	84/78
Isobutyl methacrylate	52/50
Methyl acrylate	33/29
n-Butyl acrylate	18/15
Styrene	91/85

For example, with formic acid a comparable total yield of around 70% is obtained for both catalysts. With acetic acid however, up to 82% of total conversion is reached with the heterogeneous system **4**, whereas the homogeneous system **1** only reaches 76% total yield for the addition of acetic acid to octadiyne. Besides the formation of the (*E*)-alk-1-enyl ester, also a small percentage of (*Z*)-alk-1-enyl ester, Markovnikov addition products and disubstituted enol esters are obtained.

When phenylacetylene is used as the alkyne source, the dimerization reaction that was mentioned in the Introduction becomes very important. With compound **4**, almost no nucleophilic addition of the carboxylic acid to the triple bond occurs and the (*E*)-enyne is formed with a selectivity of at least 85% reaching an almost quantitative total yield and this occurs for both acids. Compound **1** shows totally different behaviour. When using phenylacetylene, the outcome of the reaction depends on the carboxylic acid used. With formic acid, this system forms selectively the (*E*)-alk-1-enyl ester. Performing the reaction with acetic acid leads to the stereoselective formation of the (*E*)-enyne. In this case, system **1** reaches an excellent total yield of 96% and a selectivity of 78% for the formation of the (*E*)-enyne.

To our knowledge, system **4** is the most active heterogeneous ruthenium catalyst reported so far for (i) the selective formation of (*E*)-alk-1-enyl esters from alkadiynes and saturated carboxylic acids and (ii) the selective dimerization of mono-alkynes into the corresponding (*E*)-enyne.

3.2.6. Stability and recycling of the heterogeneous hybrid catalyst. For the heterogeneous catalyst we also tested the stability (test reaction is ROMP using norbornene as a substrate, reaction conditions: monomer/Ru/TMSD = 100/1/2, 2 ml of toluene, 85 °C, 1 h). Stability of a supported heterogeneous catalyst under reaction conditions means (i) no leaching of the active species into solution and (ii) no degradation of the active form of the catalyst during reaction. To test this we added a second portion of substrate to the completely polymerised system. This second polymerization was also quantitative. Even after adding a fifth portion of NBE the conversion was still 92%. These results show that the active site of the catalyst remains intact during the above-mentioned test and that no diffusion limitations occur under these test conditions. To test the leaching of the catalytic system we filtered off the catalyst after terminating the reaction mixture as described in the Experimental section (reaction conditions: monomer/Ru/TMSD = 50/1/2, 5 ml toluene, 85 °C, 1 h). After drying the catalyst *in vacuo* for 1 night a sample for XRF analysis was taken. The XRF measurement reveals that the Ru content of the MCM-41 was the same as before polymerization (the variability on XRF analyses is around ±6% of the measured value), indicating that possible leaching was below the detection limit. The recycling capabilities of our heterogeneous hybrid catalytic system were tested in RCM experiments. As a test substrate we used diethyldiallyl malonate. The procedure followed to study the reusability of the heterogeneous catalyst was the following: after 2 hours of reaction the catalyst was filtered off under nitrogen atmosphere, dried *in vacuo* for 2 hours and tested again (the other reaction condition parameters are the same as mentioned in the Experimental section). Whereas the first run gives a conversion of 100%, the second, the third and the fourth runs give conversions of respectively 98%, 96% and 96% after 1 hour of reaction. In 1998 Sheldon *et al.*[16] highlighted that the conventional practice of recycling a heterogeneous catalyst without observing any significant loss of activity is in fact no proof of heterogeneity. It appears now commonplace for true heterogeneity to be tested by filtering the heterogeneous catalyst at the reaction temperature (before completion of the reaction) and testing the filtrate for activity. When we applied this procedure to a RCM experiment with diallylphthalate (reaction conditions the same as mentioned in the Experimental section, but the reaction was stopped after 4 hours), we observed that the filtrate showed no further RCM activity, as no further increase of the conversion was observed, even after keeping the filtrate for an additional 17 hours at 85 °C.

4. Conclusion

In conclusion, we succeeded in synthesising a stable and recyclable heterogeneous catalyst that was also fully characterised. Moreover, filtrate tests and XRF measurements reveal negligible leaching of the active species from the carrier. Despite the somewhat lower conversions of the heterogeneous system in comparison with the homogeneous system in ROMP reactions, the hybrid catalyst provides polymers with narrower polydispersities, indicating more controlled polymerization and diminished sensitivity of the heterogeneous system towards backbiting reactions. In RCM experiments and Karasch addition reactions, the heterogeneous catalyst shows respectively a comparable or slightly lower catalytic activity than its homogeneous counterpart. The very easy separation of the catalyst from the reaction products, however, certainly turns the scale in favour of the hybrid heterogeneous system.

Table 6 Vinylation reactions of some representative substrates using catalytic systems **1** and **4**[a]

			Total yield (%)	% M.	% anti-M.(*Z*)	% anti-M.(*E*)	% head-to-tail enyne	% (*Z*)-enyne	% (*E*)-enyne
1	ph.ac.	f. ac.	74	12	—	79	—	4	5
		ac.ac.	96	3	2	9	3	5	78
4	ph.ac.	f. ac.	99	2	—	8	—	5	85
		ac.ac.	93	—	—	6	—	2	92
							% disubstituted enol ester		
1	octad.	f. ac.	71	11	6	76	7		
		ac.ac.	76	13	5	79	3		
4	octad.	f. ac.	70	16	6	74	4		
		ac.ac.	82	14	3	78	5		

[a] ph.ac. = phenylacetylene, octad. = octadiyne, f.ac. = formic acid, ac.ac. = acetic acid, % M. = percentage Markovnikov addition product, % anti-M. = percentage anti-Markovnikov addition product.

For ATRP reactions the immobilisation of the homogeneous system does not lead to any advantages for the obtained polymers. To conclude, vinylation experiments reveal that system **4** is the most active heterogeneous ruthenium catalyst reported so far for (i) the selective formation of (*E*)-alk-1-enyl esters out of alkadiynes and saturated carboxylic acids and (ii) the selective dimerization of mono-alkynes into the corresponding (*E*)-enyne.

Taking into account economical and environmental considerations, the handling of immobilised Ru complexes presents many advantages, such as easier separation and recovery from the reaction mixture thus enhancing recycling possibilities. In this perspective the above-mentioned hybrid catalytic system holds great promise for eco-friendly synthesis of organic intermediates.

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