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Hoveyda–Grubbs first generation type catalyst immobilized on mesoporous molecular sieves

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ABSTRACT

New heterogeneous, reusable catalysts for olefin metathesis have been prepared by immobilizing the Hoveyda–Grubbs first generation type alkylidene (commercially available as the Zhan catalyst-1C) on siliceous mesoporous molecular sieves with different pore sizes and architectures (SBA-15, SBA-16, MCM-41 and MCM-48) having the surface modified with molecules bearing dicyclohexylphosphine (PCy_2) end groups. Resulting novel heterogenized catalysts proved high activity in ring-closing metathesis (RCM) of 1,7-octadiene, diethyl diallylmalonate, tert-butyl *N*,*N*-diallylcarbamate and *N*,*N*-diallyl-2,2,2-trifluoroacetamide, in homometathesis of 1-decene, 5-hexenyl acetate and methyl 10-undecenoate, and in cross-metathesis (CM) of allylbenzene with cis-1,4-diacetoxy-2-butene. The catalytic activity decreased with decreasing pore size of supports in the order SBA-15 > MCM-48 > SBA-16 and MCM-41. Filtration test suggested that the solid catalyst was responsible for the catalytic activity. Catalysts were easily separated from the reaction mixtures and products of low levels of Ru concentration were obtained.

1. Introduction

Olefin metathesis is a very powerful, efficient and versatile method for the formation of new C=C double bonds, which has been widely used by organic chemists for the preparation of a great variety of organic compounds including natural products and special polymers [1,2].

The discovery of stable transition metal alkylidene complexes inspired the development of a new family of metathesis catalysts with high activities and tolerant to a broad spectrum of functional groups [3]. The most popular metathesis catalysts are tungsten and molybdenum alkylidene complexes developed by Schrock et al. [4] and ruthenium alkylidene complexes developed by Grubbs et al. [5]. These complexes are soluble in reaction media, which complicates receiving of products free of catalyst residues. Usually, additional purification methods must be employed for obtaining products of low transition metal concentration, which is required in many fields of metathesis application [6]. Immobilization of the soluble transition metal catalysts on a solid support is a known method how to overcome this shortage [7,8]. Hybrid catalysts prepared in this way allow an easy separation of catalysts from products, enable catalyst reusing and the employment of continuous flow processes.

Various supports such as polymers [9], monolithic gels [10], silica [11–13], mesocellular foam [14], and mesoporous molecular sieves [15–17] have been used for the immobilization of alkylidene complexes mentioned above. Mesoporous molecular sieves [18] (MMS) are siliceous materials with well-defined regular architectures, large surface areas, large void volumes and narrow pore size distributions of mesopores. Their relatively large pores facilitate mass transfer and high surface areas allow a high concentration of active sites per mass of support. They represent progressive supports for new heterogeneous catalysts for many reactions including olefin metathesis and metathesis polymerization [19,20].

Several methods for immobilization of frequently used Ru-alkylidenes (Grubbs and Hoveyda–Grubbs complexes, Scheme 1) on siliceous supports were reported [9,21,22]. The simplest method is the direct interaction of the alkylidene complex with the support surface. There are several reports on the immobilization of Hoveyda–Grubbs 2nd generation alkylidene (complexes **III**, Scheme 1) using this way [16,23–25]. The details about the interaction mode are not yet known; adsorption and/or hydrogen bonds are assumed. In spite of high activity the effective application of these catalysts seems to be limited by the polarity of solvent used. In hexane and cyclohexane the Ru leaching into liquid phase was

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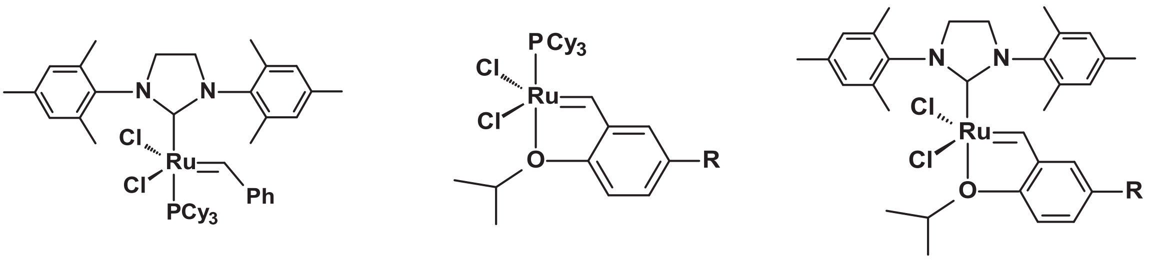


I

Grubbs 2nd Gen.

II₀, II

R = H, Hoveyda-Grubbs 1st Gen. - II₀
R = SO_2NMe_2, RC-304 (Zhannan Pharma) - II

III₀, III

R = H, Hoveyda-Grubbs 2nd Gen. - III₀
R = SO_2NMe_2, RC-303 (Zhannan Pharma) - III

Cy = cyclohexyl

Scheme 1. Grubbs and Hoveyda–Grubbs commonly used catalysts.

very low (e.g. 0.04% of Ru content in catalyst used) but in aromatic solvents it increased by two orders of magnitude and in dichloromethane the leaching of 14% was observed [16].

The most frequently used immobilization methods consist in the exchange reaction between complex ligands and suitable reactive groups on the surface providing covalently bound metal species. For Ru alkylidenes (Grubbs and Hoveyda–Grubbs complexes, Scheme 1), the replacement of Cl ligands (by a carboxylate) [13,26–28], NHC ligands [29–33], and alkylidene ligands [34,35] by special linkers have been studied, which usually required elaborate organic syntheses. In the case of alkylidene ligand exchange, the recapturing of propagating alkylidenes on the surface was assumed (so call boomerang catalysts), the extent of which is still a matter of a debate [36,37]. Immobilization of the second generation Grubbs catalyst (complex **I**, Scheme 1) via an exchange of phosphine ligands has been successful recently [38]. The support modification with commercially available phosphine linkers as well as the ligand exchange proceeded easily and heterogeneous catalysts prepared exhibited a high activity and selectivity in metathesis reactions (RCM, ROMP and cross-metathesis). Although dissociation of phosphine ligand is considered as a prerequisite for the initiation process [39], filtration experiments did not show any considerable leaching of the active species into the liquid phase and the catalysts were reusable for several times. The content of Ru in the products varied according to the experimental conditions in the range from 162 ppm to 5.8 ppm [38]. Hoveyda–Grubbs first generation alkylidene (complexes $\mathbf{II_0}$, **II**, Scheme 1) has not been immobilized via phosphine exchange, according to our best knowledge. In fact, these complexes should be bound more firmly to the surface than complex **I**, since the initiation proceeds by opening the chelate alkylidene ligand [39,40].

The aim of this contribution is to report on (i) the preparation of heterogeneous metathesis catalysts by the immobilization of a Hoveyda–Grubbs first generation type complex **II** on mesoporous molecular sieves (SBA-15, SBA-16, MCM-41, and MCM-48) via exchange of phosphine groups (Scheme 2), (ii) the activity of prepared catalysts in metathesis reactions of different substrates, (iii) Ru leaching and the possibility of catalyst reuse, and (iv) the influence of the supports used on the catalyst activity. The work was done with the complex **II**, because it is known that the electronic effect of dimethylaminosulfonyl substituent on isopropoxybenzylidene ligand increases activity of Hoveyda–Grubbs catalysts substantially [28,41]. As supports, mesoporous molecular sieves of different pore sizes and architectures have been used: (i) SBA-15 and MCM-41 having hexagonal channel-like structures and mesopore diameters 6.2 and 4.0 nm, respectively, (ii) SBA-16 of a cage-like body-centered-cubic structure with pore cage diameter of 7.4 nm and pore entrance diameter 4.7 nm, and (iii) MCM-48 of a three-dimensional interconnected cubic pore structure with mesopores of 6.0 nm.

2. Experimental

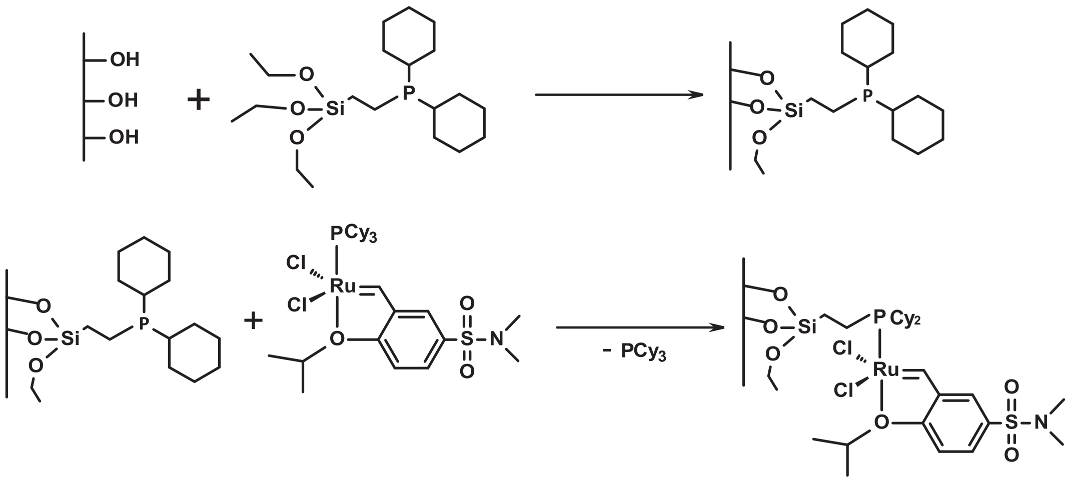
2.1. Materials and techniques

Siliceous SBA-15, SBA-16, MCM-41 and MCM-48 were prepared according to the literature [42–44]. Toluene (Lach-Ner, Czech Rep.) was dried overnight over anhydrous Na_2SO_4, then distilled with Na and stored over molecular sieve 4A. Dichloromethane (Lach-Ner) was dried overnight over anhydrous $CaCl_2$ then distilled with P_2O_5. 2-(Dicyclohexylphosphine)ethyltriethoxysilane (ABCR, 95%) was used as obtained. 1,7-Octadiene (Fluka, purity ≥ 97%), diethyl diallylmalonate (Sigma–Aldrich, 98%), allylbenzene (Aldrich, 98%), cis-1,4-diacetoxy-2-butene (Aldrich, 95%), *N*,*N*-diallyl-2,2,2-trifluoroacetamide (Aldrich, 98%), tert-butyl *N*,*N*-diallylcarbamate (Aldrich, 98%), 5-hexenyl acetate (Aldrich, 97%), 1-decene (Fluka, 98%), methyl 10-undecenoate (Aldrich, 96%), were used after passing through a column of activated alumina. Cyclooctene (Janssen Chimica, 95%) was distilled from CaH_2. The Ru complex **II** was purchased from Zannan Pharma, Ltd., China.

Textural parameters of supports and catalysts were determined using nitrogen adsorption isotherms at −196 °C with a Micromeritics ASAP 2020 instrument. All the materials were outgassed before adsorption measurement using a program starting from ambient temperature to 110 °C (heating ramp of 0.5 °C/min) until the residual pressure of 1 Pa was reached. The sample was outgassed at this temperature under turbomolecular pump vacuum for 8 h. X-ray powder diffraction (XRD) data were obtained on a Bruker AXS D8 Advance diffractometer with a graphite monochromator and a position sensitive detector Våntec-1 using Cu Kα radiation (at 40 kV and 30 mA) in Bragg–Brentano geometry.

^{31}P MAS (Magic-Angle Spinning) and ^{29}Si MAS nuclear magnetic resonance (NMR) spectra were recorded on a 500 MHz (11.7 T) Wide Bore Agilent NMR system using an Agilent 3.2 mm T3 HXY MAS Solids NMR Probe and zirconia rotors. Sample rotation frequencies for ^{29}Si cross-polarization (CP MAS) experiments were 10 kHz while for ^{31}P MAS experiments were 20 kHz. Recycle delays and number of transients for ^{31}P MAS and ^{29}Si CP MAS were 30 s and 400, 5 s and 10,000, respectively. The chemical shifts reported are expressed relative to TMS and 80% solution of H_3PO_4 for ^{29}Si and ^{31}P signals, respectively.

Photoelectron spectra of the samples were measured using an ESCA 310 (Scienta, Sweden) spectrometer equipped with a hemispherical electron analyzer operated in a fixed transmission mode. Monochromatic Al Kα radiation was used for electron excitation. The spectra were recorded at room temperature. The Si 2p, O 1s,



Scheme 2. Immobilization of **II** on mesoporous supports.

Cl 2p, P 2p, P 2s, C 1s, and Ru 3d photoelectrons were measured. Sample charging was corrected using the Si 2p peak at 103.4 eV as an internal standard. For overlapping C 1s and Ru 3d lines, the contributions of individual components were determined by curve fitting.

Ruthenium and phosphorus determination was performed by inductively coupled plasma mass spectrometry (ICP-MS) using Elan DRC-e (Perkin–Elmer, Concord, Canada) spectrometer, equipped with a concentric PTFE nebulizer, a cyclonic spray chamber and a high efficiency quartz torch. Before measurement the liquid samples were evaporated to dryness and mineralized with HNO_3 in UniClever microwave decomposition unit (Plazmatronika-Service, Wroclaw, Poland). Solid samples containing silica were decomposed with the mixture of HF and HNO_3 (1:3, v/v). The estimation error was 5%.

2.2. Catalyst preparation

The modification of mesoporous molecular sieves (predried under vacuum at 300 °C for 3 h) by 2-(dicyclohexylphosphine)ethyltriethoxysilane was performed in toluene at 60 °C under argon atmosphere. In a typical modification, 15 mL of toluene was added to 1100 mg of SBA-15 in a Schlenk tube, then 690 mg of 2-(dicyclohexylphosphine)ethyltriethoxysilane was added, and the mixture was stirred for 23 h at 60 °C. The product was 3 times washed under argon atmosphere with 10 mL of toluene and finally the rest of toluene was removed by drying of the modified SBA-15 in vacuum at room temperature. The modified sieves were stored under argon atmosphere. The modification of SBA-16, MCM-41 and MCM-48 was made in the same way. The content of P in modified sieves was 1.3 wt.% of P. The immobilization of Hoveyda–Grubbs catalyst **II** on modified mesoporous molecular sieves was carried out in toluene at room temperature under argon atmosphere. Preparation of catalyst **II**/SBA-15: 15 mL of toluene was added to 500 mg of SBA-15 modified with PCy_2 linkers, then 45.5 mg of Hoveyda–Grubbs 1st generation complex **II** (Scheme 2) was added and the suspension was stirred for 24 h. The product was 2 times washed under argon atmosphere with 10 mL of toluene and 3 times washed with 10 mL of dichloromethane. The rest of the solvent was removed by drying the catalyst in vacuum at room temperature. Catalysts **II**/SBA-16, **II**/MCM-48, and **II**/MCM-41 were prepared in a similar way (amounts of sieves and complexes are given in Table 1). The catalysts were stored in dried glass tubes sealed under argon atmosphere. All manipulations with catalysts and catalytic experiments were carried out under argon atmosphere using standard Schlenk tube technique.

2.3. Metathesis reactions

Metathesis reactions were performed under Ar atmosphere in a Schlenk tube equipped with a magnetic stirring bar. In a typical RCM experiment, 23 mg of the catalyst **II**/SBA-15 was placed into the reactor, then 1.6 mL of toluene was added, and the suspension was heated to 30 °C. Then 37 μL of 1,7-octadiene (molar ratio 1,7-octadiene:Ru = 100, c^0 (1,7-octadiene) = 0.15 mol/L) was added under stirring. In a typical cross-metathesis (CM) experiment, 22.0 mg of catalyst **II**/SBA15 was placed into the reactor, then 2.5 mL of toluene was added, and the suspension was heated to 80 °C in an oil bath. Then the mixture of 74 μL of allylbenzene (AllB), 179 μL of cis-1,4-diacetoxy-2-butene (DAB) (molar ratio AllB/Ru = 40, c^0 (AllB) = 0.2 mol/L, c^0 (DAB) = 0.3 mol/L) and 70 μL of *n*-nonane (internal standard) was added under stirring. During metathesis experiments samples (0.1 mL) were taken in given intervals after substrate(s) addition. Ethyl vinyl ether (terminating agent) was added into each sample, the samples were centrifuged, and the supernatant analyzed by GC. A high-resolution gas chromatograph Agilent 6890 with DB-5 column (length: 50 m, inner diameter: 320 μm, stationary phase thickness: 1 μm) was used for reaction product analysis. *n*-Nonane was used as an internal standard, whenever required. Individual products were identified by GC/MS (ThermoFinnigan, FOCUS DSQ II Single Quadrupole). The RCM experiment was repeated 3 times and the absolute error in the determination of conversion was ±2%. The catalyst activity was expressed in TOF at 5 min (TOF_5) for homogeneous experiments and in TOF at 30 min for heterogeneous catalysts. TOF values were calculated with respect to the amount of Ru. In the case of ring-opening metathesis polymerization (ROMP) of cyclooctene (COE), the high molecular weight product was precipitated in methanol, dried in vacuum at 60 °C and the yield was determined gravimetrically. Molecular weight of polymer was determined by SEC.

3. Results and discussion

3.1. Catalyst preparation

Mesoporous molecular sieves used as catalyst supports exhibited characteristics of highly ordered materials with narrow pore size distribution, as it can be seen from X-ray diffraction patterns and nitrogen adsorption isotherms (both in Supporting

Table 1
Amounts of modified sieves and Ru complexes used for the preparation of the catalysts.

Catalyst	Used supports	Weight of P modified sieves (mg)	Weight of II applied (mg)	Catalyst Ru content (wt.%)	*f*
II/SBA-15	SBA-15	1200	109.2	1.07	0.83
II/MCM-48	MCM-48	720	65.5	1.01	0.78
II/MCM-16	SBA-16	340	47.6	0.95	0.48
II/MCM-41	MCM-41	550	50.3	1.06	0.82

f = fraction of Ru captured on the support.

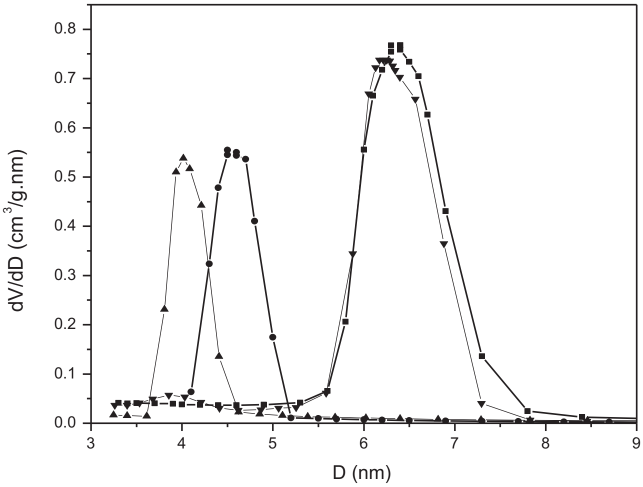


Fig. 1. Pore size distribution for SBA-15 (■), SBA-16 (●), MCM-41 (▲) and MCM-48 (▼).

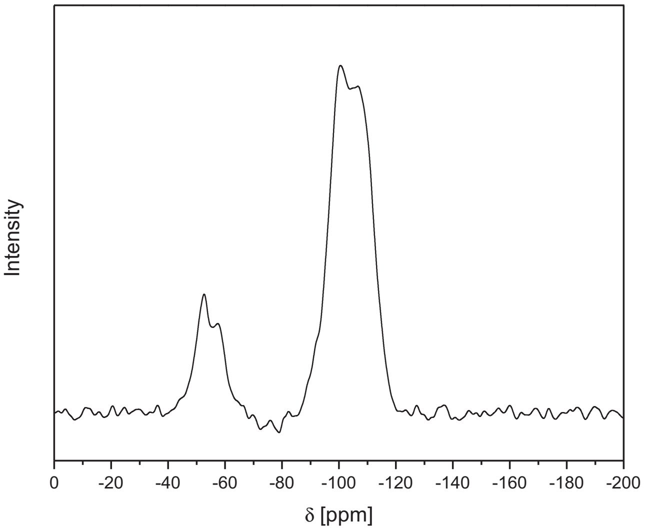


Fig. 2. ^{29}Si CP MAS NMR spectra of SBA-15 with PCy_2 linkers.

Information, Figs. S1 and S2, respectively) and Fig. 1. The textural parameters are collected in Table 2. All materials have large specific surface area (S_{BET} from 756 to 952 m^2/g), high void volume (V from 0.61 to 1.14 cm^3/g) and average pore size diameter D increasing in the order MCM-41 < SBA-16 < MCM-48 < SBA-15 from 4.0 nm to 6.2 nm. According to SEM images, the support grain is between 1 and 5 μm (see Supporting Information, Fig. S3).

Modification of mesoporous molecular sieves with PCy_2 linkers was carried out via reaction of surface OH groups with ethoxysilyl groups of 2-(dicyclohexylphosphino) ethyltriethoxysilane (see Scheme 2). The amount of P in modified sieves was 1.3 wt.% according to the elemental analysis. Fig. 2 shows ^{29}Si CP MAS NMR spectra of SBA-15 modified with PCy_2 linkers. The presence of signals in the range from about −45 ppm to −60 ppm (T^m sites) confirms the attachment of linkers to the surface by siloxane bridges. As for T^m sites [($T^m = RSi(OSi)_m(OEt)_{3-m}$, m = 1,2,3] the values of chemical shifts corresponding to T^1, T^2 and T^3 are −47, −57 and −67 ppm, respectively [45], we can assume that in our case the PCy_2 linkers are bound to the surface by T^1 and T^2 sites. The linker density, calculated from the P concentration, is 0.42 linkers/nm^2. Assuming that the average OH group concentration is about 4.2 OH groups/nm^2 for all sieves [46], only 1/10 of OH groups was consumed for the reaction with PCy_2 linkers. The possibility of phosphine oxidation by reaction with surface OH groups was suggested by Fontaine et al. [47]. The ^{31}P MAS NMR spectrum of SBA-15 modified with PCy_2 linkers (Fig. 3) really shows resonances in the region 50–60 ppm, which can be ascribed to oxidized P product(s). Nevertheless, the dominant singlet at 2.6 ppm proved that

Table 2
Textural parameters of supports and catalysts.

Supports and catalysts	S_{BET} (m^2/g)	V_{ME} (cm^3/g)	D_{ME} (nm)
SBA-15	766	1.03	6.2
SBA-15 modified with linkers	431	0.68	6.2
II/SBA-15	474	0.71	5.9
SBA-16	796	0.61	7.4[a]4.7[b]
II/SBA-16	341	0.23	3.7[b]
MCM-48	756	0.91	6.0
II/MCM-48	523	0.61	5.2
MCM-41	972	1.14	4.0
II/MCM-41	701	0.64	3.9

[a] Pore cage diameter.
[b] Pore entrance diameter.

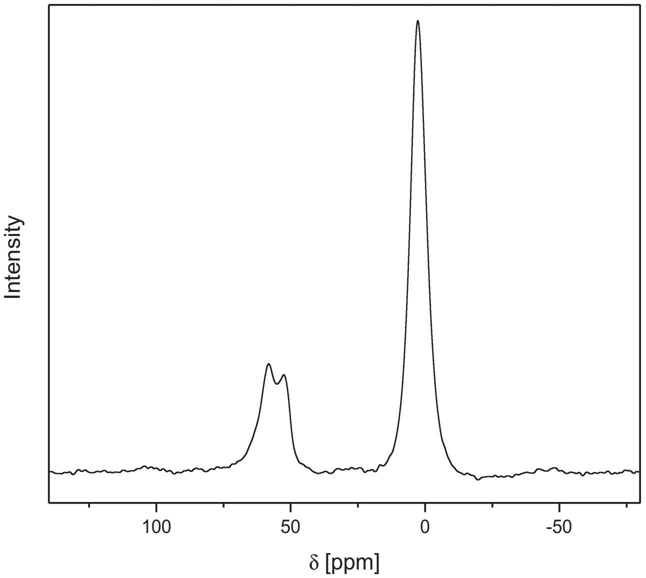


Fig. 3. ^{31}P MAS NMR spectra of SBA-15 modified with PCy_2 linkers.

Table 3
XPS binding energies (±0.2 eV) for complexes and catalysts used.[a]

Sample	Ru $3d_{5/2}$	C 1s	Cl 2p	P 2s
II	281.2	284.8	198.2	188.5
SBA-15 modified	–	284.8	–	189.7
II/SBA-15	280.4	284.8	198.3	189.5

[a] The line C 1s (284.8 eV) was used as a reference for spectra calibration.

the majority of P is in the phosphine state being able to react with Ru alkylidene by phosphine ligand exchange.

The results of the immobilization of Ru complex **II** on the modified sieves (see Scheme 2) are described in Table 1. The catalysts labeled according the support used as **II**/SBA-15, **II**/MCM-48, **II**/SBA-16, and **II**/MCM-41 were prepared. The immobilization was not quantitative under the conditions applied and the fractions of Ru captured on the sieves (**f**) differed according to the sieve architecture – the highest being for hexagonal SBA-15 and MCM-41 (0.83, 0.82, respectively) and the lowest for cubic cage-like SBA-16 (0.48). As a result, different amounts of **II** had to be used for obtaining the catalyst of the approximately same Ru loadings (1 wt.%). XRD as well as nitrogen adsorption measurements confirmed that the support structure was preserved in all catalysts (see Supporting Information, Figs. S4 and S5). The textural parameters of catalysts are compared with those of parent and/or P modified supports in Table 2. As expected, the introduction of organic linkers into the pores of supports resulted in decreased nitrogen adsorption capacity. It is reflected by significantly lower S_{BET} values and reduced pore volumes as compared with the parent supports (see Table 2). Subsequent immobilization of complex **II** led only to small changes in textural parameters, because of a low amount of complex introduced (Table 2). For catalyst function it is important that the changes of average pore diameter are rather small (for SBA-15 and MCM-41 nearly negligible).

The XPS results are in agreement with **II** immobilized according to Scheme 2. The stoichiometry for SBA-15 modified with P linkers and for catalyst **II**/SBA-15 calculated from XPS were $\mathrm{Si_{1.0}O_{1.97}P_{0.042}C_{0.92}}$ and $\mathrm{Si_{1.0}O_{1.95}Ru_{0.008}Cl_{0.015}P_{0.046}C_{0.99}}$, respectively. The Ru/P ratio shows the excess of P indicating that only about 20% of P linkers participated in the Ru immobilization. Si/P ratios for modified support and catalyst should be the same according to Scheme 2. A slight increase in P concentration in catalyst might be connected with a partial trapping of liberated $\mathrm{PCy_3}$ in the sieves as it was recently described [47]. The XPS binding energies for complexes **II**, SBA-15 modified support and catalyst **II**/SBA-15 are provided in Table 3. Binding energies for complex **II** are in agreement with the values of Jarzembska et al. [48] (taking into account the difference in values of C1s binding energy used for spectra calibration). The increase in the binding energy of P 2s and P 2p for **II**/SBA-15 in comparison with **II** can be ascribed to the dominating contribution of free P linkers in **II**/SBA-15. A lower value of binding energy of Ru $3d_{5/2}$ electrons in **II**/SBA-15 in comparison with that in the free complex **II** may be connected with the changes in geometry of Ru coordination sphere as a result of the immobilization. Similar changes have already been observed for the immobilization of **I** on mesoporous molecular sieves via phosphine ligand exchange [38].

3.2. Catalytic activity

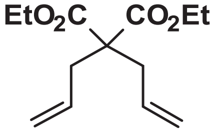
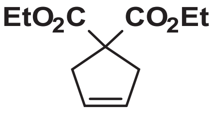
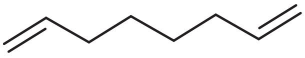
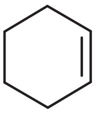
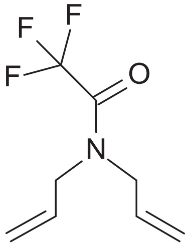
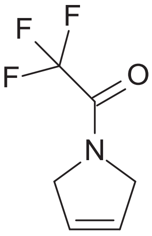
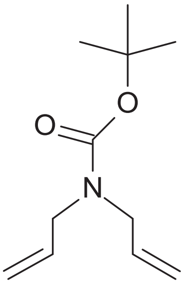
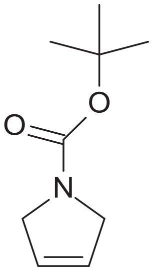
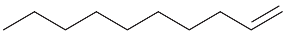
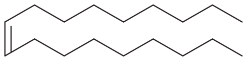
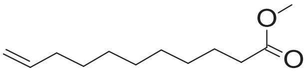
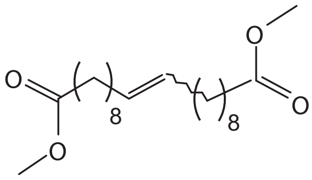
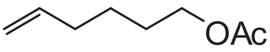
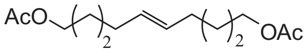
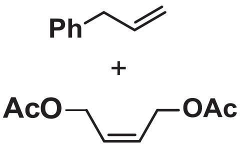
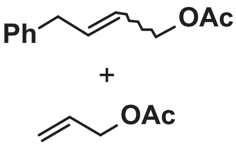
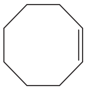
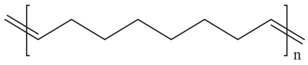
The catalytic activity was tested in (i) RCM of 1,7-octadiene, diethyl diallylmalonate (DEDAM), *N*,*N*-diallyl-2,2,2-trifluoroacetamide (DAF), and tert-butyl *N*,*N*-diallylcarbamate (DAC), (ii) metathesis of 1-decene, 5-hexenyl acetate, and methyl 10-undecenoate, (iii) cross-metathesis of cis-1,4-diacetoxy-2-butene (DAB) with allylbenzene (AllB), and (iv) ROMP of cyclooctene. The results achieved with **II**/SBA-15 are summarized in Table 4. For substrate/Ru molar ratio = 100, RCM of 1,7-octadiene proceeded smoothly giving high conversions even at low reaction temperatures (84% at 0 °C and 98% at 30 °C). On the other hand, RCM of DEDAM required reaction temperature 80 °C to obtain 90% conversion. Selectivity in all RCM reactions was very high (95–100%, see Table 4). The products of cycloisomerization (diethyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate for DEDAM, 1-(trifluoroacetyl)-3-methyl-4-methylenepyrrolidine for DAF) were observed as the only side products. The side product of RCM of DAC was not identified.

In metathesis of 1-decene, 5-hexenyl acetate, and methyl 10-undecenoate lower conversions were reached (57%, 77%, and 64%, respectively). As ethylene was removed from the reaction mixture, higher conversions were expected. It should be noticed that approximately the same incomplete conversions were achieved for these three substrates using **II** as a homogeneous catalyst under same reaction conditions (see conversion curves in Supporting Information, Figs. S6–S8). The shape of conversion curves for **II** shows a strong retardation of the reactions at prolonged reaction times suggesting a gradual catalyst deactivation. The inherent deactivation of Hoveyda–Grubbs catalyst was described and reaction mechanisms were outlined [3,49,50]. As concerns selectivity, double bond shift isomerization followed by cross-metathesis is responsible for the formation of small amounts of side products (heptadecene, 1,9-diacetoxynonene, dimethyl 1,19-nonadecenedioate for metathesis of 1-decene, 5-hexenyl acetate and 10-undecenoate, respectively). In cross-metathesis of DAB with AllB a 1.5-fold excess of DAB was used to reduce the homometathesis of AllB to 1,4-diphenyl-2-butene (Scheme 3). With **II**/SBA-15, AllB and DAB conversions achieved (33% and 23%, respectively) are lower in comparison with the homogeneous experiment (53% for AllB and 33% for DAB; see Supporting Information, Fig. S9). However, the selectivity for cross-metathesis product was approximately the same (79% for **II**/SBA-15 and 81% for **II**). The main by-product was formed by homometathesis of allylbenzene (1,4-diphenyl-2-butene). In ROMP of COE (COE/Ru molar ratio = 500), catalyst **II**/SBA-15 provided high molecular weight polymer ($M_w = 160{,}000$, $M_n = 84{,}000$) in 74% yield.

Fig. 4a and b shows conversion curves of RCM of 1,7-octadiene with homogeneous catalyst **II** and heterogeneous catalysts **II**/SBA-15, **II**/MCM-48, **II**/SBA-16, and **II**/MCM-41 in toluene at 0 °C (Fig. 4a) and 30 °C (Fig. 4b). At 0 °C a strong increase in initial reaction rates (expressed by $\mathrm{TOF_{30}}$ and $\mathrm{TOF_5}$ values, respectively) in the order **II**/MCM-41 ($\mathrm{TOF_{30}} = 0.002\ \mathrm{s^{-1}}$) ≤ **II**/SBA-16 ($\mathrm{TOF_{30}} = 0.004\ \mathrm{s^{-1}}$) < **II**/MCM-48 ($\mathrm{TOF_{30}} = 0.010\ \mathrm{s^{-1}}$) ≤ **II**/SBA-15 ($\mathrm{TOF_{30}} = 0.012\ \mathrm{s^{-1}}$) < **II** ($\mathrm{TOF_5} = 0.143\ \mathrm{s^{-1}}$) was observed. Conversion values achieved after 5 h reaction increased in the same way. This may reflect the influence of diffusion rate in catalyst pores on the initiation and/or propagation step of the catalytic process. Raising the temperature to 30 °C reaction rates of all catalysts increased considerably and the differences between individual heterogeneous catalysts was suppressed. Although the initial reaction rates of heterogeneous catalysts ($\mathrm{TOF_{30}} = 0.030\ \mathrm{s^{-1}}$) remained lower than that of **II** ($\mathrm{TOF_5} = 0.290\ \mathrm{s^{-1}}$), the conversion after 5 h is the same for all catalyst (98%).

The effect of support pore size on catalyst activity has already been observed [17,19]. As concerns immobilized Ru alkylidenes, the increasing activity with increasing pore size was found for RCM of citronellene [24] and for metathesis of methyl oleate [38]. In addition, three-dimensional pore systems (MCM-48, SBA-16) can be more advantageous for molecular diffusion than one-dimensional channel-like pore systems (MCM-41 and SBA-15) [51]. Locating Hoveyda–Grubbs alkylidene into confined space of cage-like system contributed to catalyst stability and prolonged its life time [25]. In our case, the pore size seems to be decisive. For SBA-16 the entrance diameter (4.7 nm) is more important for catalyst activity

Table 4
Application of catalyst **II**/SBA-15 in various metathesis reactions.

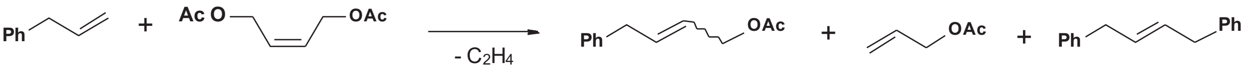
Reactant	Product	Conditions	Conversion	Selectivity
		t = 80 °C	90%	95%
		t = 0 °C (30 °C)	84% (98%)	100%
		t = 30 °C	93%	98%
		t = 30 °C	92%	98%
		t = 80 °C	57%	97%
		t = 80 °C	64%	98%
		t = 80 °C	77%	95%
		t = 80 °C[a]	33% to AllB and 23% to DAB	79%[b]
		t = 80 °C[c]	Polymer yield = 74%	–

Reaction conditions: toluene, Ru/substrate =1:100, c^0 substrate= 0.15 mol/L, reaction time 5 h.

[a] c^0 DAB = 0.3 mol/L, c^0 AllB = 0.2 mol/L, Ru/DAB + AllB = 1:100.

[b] Selectivity was calculated with respect to CM products.

[c] Ru/COE = 1:500, c^0 COE = 0.8 mol/L, reaction time 3 h.



Scheme 3. Cross-metathesis of allylbenzene with cis-1,4-diacetoxy-2-butene.

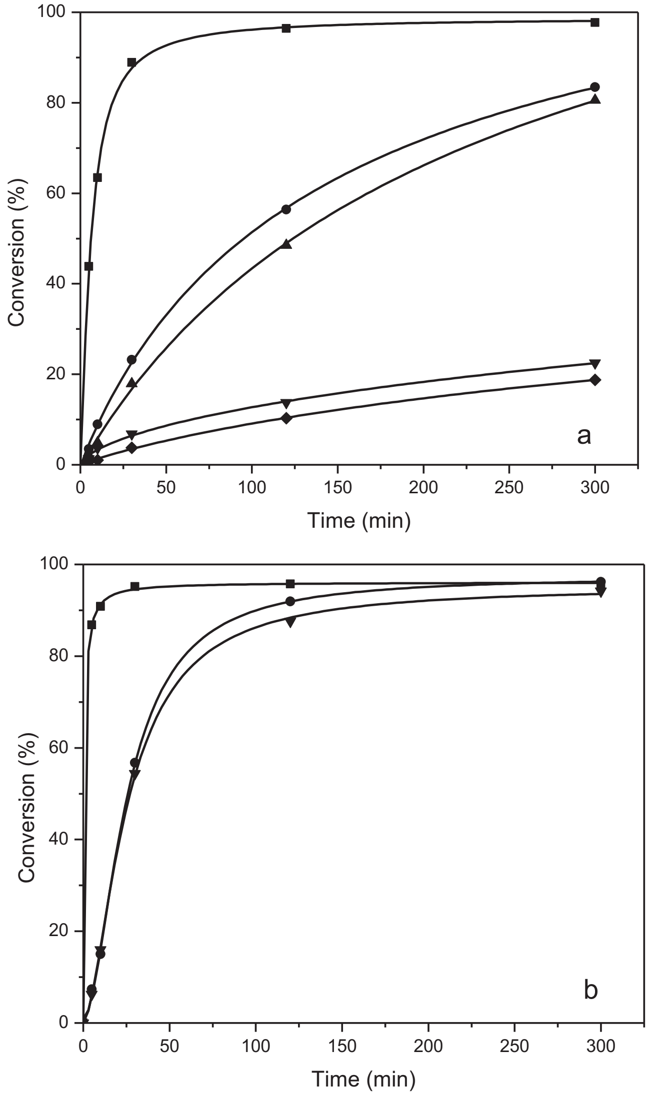


Fig. 4. RCM of 1,7-octadiene with catalysts **II** (■), **II**/SBA-15 (●), **II**/MCM-48 (▲), **II**/SBA-16 (▼) and **II**/MCM-41 (♦). 0 °C (a), 30 °C (b), Ru/1,7-octadiene = 1:100, toluene, c^0 (1,7-octadiene) = 0.15 mol/L.

than the cage diameter since the initial reaction rate over **II**/SBA-16 does not exceed too much that of **II**/MCM-41 (Fig. 4a). Similarly, the reaction rates and final conversions over **II**/MCM-48 and **II**/SBA-15 are close each other, despite different architecture of their supports.

The effect of support on conversions achieved was observed also for RCM of DAF (Fig. 5) and DAC (Fig. 6). Conversions after 5 h reaction increased in the order **II**/MCM-41 < **II**/SBA-16 < **II**/MCM-48 ≤ **II**/SBA-15 ≤ **II** for DAF, and **II**/MCM-41 < **II**/SBA-16 = **II**/MCM-48 < **II**/SBA-15 ≤ **II** for DAC. This order practically followed the increasing pore size similarly as for 1,7-octadiene at 0 °C. **II**/SBA-15 and/or **II**/MCM-48 exhibited high conversions close to those of homogeneous catalyst **II**. The shape of conversion curves for less active catalysts **II**/MCM-41 and **II**/SBA-16 (in the case of DAF) may indicate that not only diffusion restriction but also catalyst deactivation during the reaction was the reason for their lower activity. The catalyst deactivation may include (i) decomposition of immobilized carbene species, described for example in Ref. [52] and (ii) accumulation of reaction products in the pores due to the hydrophilicity of catalyst surface. Both (i) and (ii) may become important when pore diameter decreases.

Filtration test helped to distinguish whether the catalytic activity is bound to the heterogeneous phase or the catalytically active species are present into liquid phase [53]. Filtration test for RCM of 1,7-octadiene over **II**/SBA-15 in toluene is shown in Fig. 7. After 5 min of the reaction, half of the liquid phase was filtered off at the reaction temperature and transferred into a parallel reactor, where it was kept under the same conditions as the parent reaction mixture in the original reactor. In the original reactor, reaction continued reaching nearly 100% of conversion, whereas in the reactor with separated liquid phase, the reaction stopped immediately. It indicates the solid catalyst is responsible for the catalytic activity in metathesis reactions studied. Similar results were obtained for **II**/SBA-15 in dichloromethane (see Supporting Information, Fig. S10).

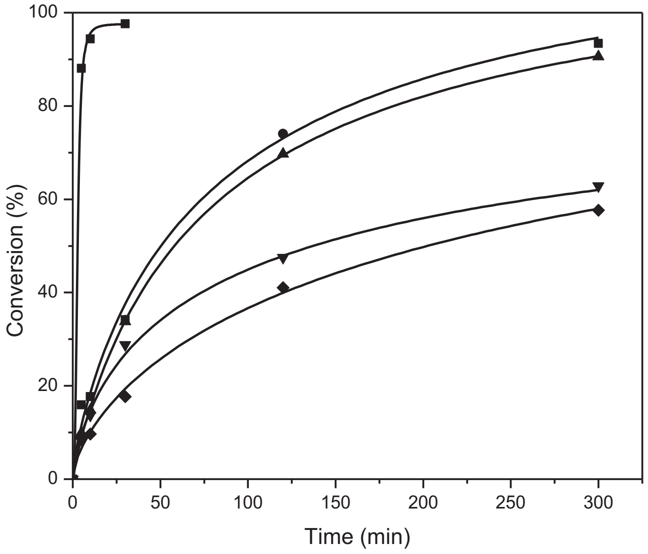


Fig. 5. RCM of *N*,*N*-diallyl-2,2,2-trifluoroacetamide (DAF) with catalysts **II** (■), **II**/SBA-15 (●), **II**/MCM-48 (▲), **II**/SBA-16 (▼) and **II**/MCM-41 (♦). 30 °C, Ru/DAF = 1:100, toluene, c^0 (DAF) = 0.15 mol/L.

As for the catalyst **II**/SBA-15, Ru leaching in the course of RCM of 1,7-octadiene in toluene (40 °C, 5 h, Ru/1,7-octadiene = 1:250, c^0 (1,7-octadiene) = 0.15 mol/L) was 0.1% of original Ru content in the catalyst corresponding to the maximum product contamination equal to 5.6 ppm of Ru. It should be noted that it is bellow the limit prescribed for pharmaceutical products (10 ppm) [54]. On the

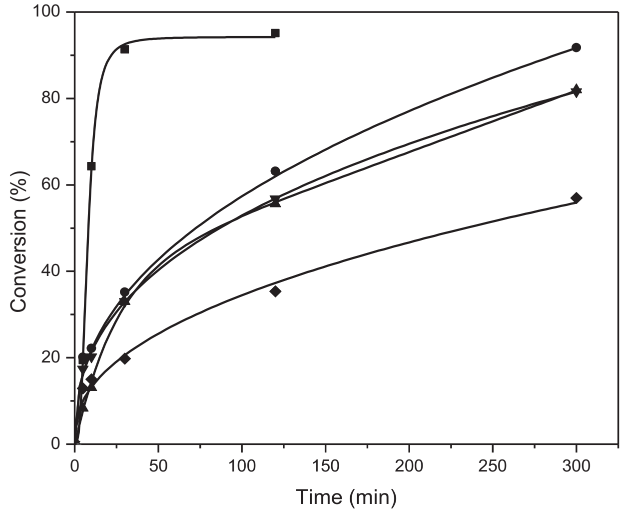


Fig. 6. RCM of tert-butyl diallylcarbamate (DAC) with catalysts **II** (■), **II**/SBA-15 (●), **II**/MCM-48 (▲), **II**/SBA-16 (▼) and **II**/MCM-41 (♦). 30 °C, Ru/DAC = 1:100, toluene, c^0 (DAC) = 0.15 mol/L.

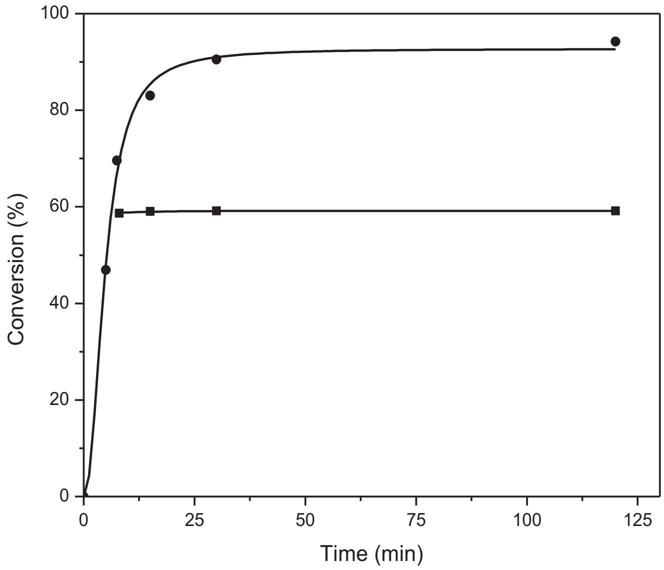


Fig. 7. Filtration experiment for RCM of 1,7-octadiene with catalyst **II**/SBA-15. Liquid phase in contact with solid catalyst (circles), liquid phase after filtration (squares), toluene, 40 °C, molar ratio 1,7-octadiene/Ru = 250, c^0 (1,7-octadiene) = 0.15 mol/L.

Table 5
Reusing of catalyst **II**/SBA-15.[a]

Runs	1	2	3	4	5	6
Conversion (%)	98.0	97.9	97.9	97.7	92.0	54.1

[a] RCM of 1,7-octadiene, 40 °C, 5 h, toluene, Ru/1,7-octadiene = 1:100, c^0 1,7-octadiene = 0.15 mol/L.

other hand, the Ru leaching increased to 2.2%, when the reaction was carried out in dichloromethane (under same temperature and concentrations as for toluene). For RCM of DEDAM in toluene (80 °C, Ru/DEAM = 1:100) the Ru leaching was 0.38% of Ru (8.0 ppm of Ru in product). It may be noticed that these values are considerably lower than those obtained for catalyst **I** immobilized through phosphine linkers (5.3% in toluene [38]) and for catalyst **III** immobilized by non-covalent interactions (4% in benzene, 14% in dichloromethane [16]).

Reusing of catalyst **II**/SBA-15 was studied in RCM of 1,7-octadiene (Table 5). After 5 h of the reaction, the catalyst was separated by filtration, washed out with toluene and new portions of toluene, and 1,7-octadiene were added. Catalyst was used 5 times without practically any decrease in conversion achieved after 5 h. Nevertheless, certain losses in catalyst amount during its separation as well as possible catalyst deactivation by ways described above caused probably the gradual decrease in catalyst activity, which was manifested in the last run.

4. Conclusions

1. Heterogenous catalysts for olefin metathesis were prepared by immobilization of commercially available alkylidene complex **II** (Zhan catalyst RC 304) on mesoporous molecular sieves SBA-15, SBA-16, MCM-41 and MCM-48 having the surface modified with PCy_2 linkers. The mesoporous character and narrow pore size distributions of supports were preserved in prepared heterogenous catalysts.
2. The catalysts (1 wt.% of Ru) proved their activity and high selectivity in RCM of 1,7-octadiene, diethyl diallylmalonate, tert-butyl *N*,*N*-diallylcarbamate and *N*,*N*-diallyl-2,2,2-trifluoroacetamide, in metathesis of 1-decene, 5-hexenyl acetate and methyl 10-undecenoate, and in cross-metathesis of allylbenzene with cis-1,4-diacetoxy-2-butene. In ROMP of COE high-molecular-weight polymer was obtained in good yield.
3. Significant effect of the support pore size on heterogeneous catalyst activity was found in RCM of 1,7-octadiene, *N*,*N*-diallyl-2,2,2-trifluoroacetamide and tert-butyl *N*,*N*-diallylcarbamate used as tested substrates. The initial reaction rates and/or conversions achieved were found to decrease with decreasing pore size of catalyst supports.
4. Filtration tests confirmed that the solid catalyst was fully responsible for the catalytic activity during the reaction. Catalyst could be easily separated from the reaction mixture in contrast to the corresponding homogeneous system and can be used repeatedly.
5. The Ru leaching was very low (0.1% of starting Ru amounts in catalyst for COE at 40 °C and 0.38% for DEDAM at 80 °C), which is about 1 order of magnitude lower than that of catalysts prepared by the immobilization of Ru alkylidene **I** on mesoporous molecular sieves through phosphine linkers.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.06.006.

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