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Hoveyda–Grubbs type metathesis catalyst immobilized on mesoporous molecular sieves—The influence of pore size on the catalyst activity

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ABSTRACT

New hybrid olefin metathesis catalysts were prepared by immobilization of Hoveyda–Grubbs type catalyst (commercially available as Zhan catalyst-1B) on the surface of mesoporous molecular sieves differing in pore size and architecture (MCM-41, MCM-48, and SBA-15) and conventional silica for a comparison. The activity of these catalysts was tested in RCM of (−)-β-citronellene, metathesis of 1-decene, ADMET of 1,9-decadiene, and in ROMP of cyclooctene and was found to increase significantly with the increasing pore size of the supports used. In all reactions, the activity of hybrid catalysts based on mesoporous molecular sieves was higher than that of catalyst using conventional silica as a support. In ROMP of cyclooctene, high molecular weight polymer ($M_w = 300{,}000$) in high yield (70–80%) was obtained with catalysts based on mesoporous supports, however, only 40% polymer yield was obtained using catalyst based on conventional silica.

1. Introduction

Olefin metathesis became an important tool in organic synthesis in last two decades [1]. Especially, the introduction of Ru alkylidenes as effective and robust catalysts (Grubbs and Hoveyda–Grubbs catalysts) enlarged the application potential of olefin metathesis considerably in the synthesis of many fine chemicals and special polymers [2,3]. Homogeneous Grubbs and Hoveyda–Grubbs type catalysts, however, have to face the problems with product separation from catalyst residues (e.g. low Ru content is required in pharmaceuticals, cosmetics, etc.) and with catalyst recovery (because of catalyst high price). Immobilization of originally homogeneous catalysts on solid supports (either organic polymers or inorganic materials) is a possible way how to solve these problems [4]. Hybrid catalysts prepared in this way should combine high activity and selectivity of parent homogeneous catalysts with easy catalyst-product separation and catalyst reusing.

Several methods have been developed for immobilization of Grubbs and Hoveyda–Grubbs type catalysts [5–10]. The most frequently used methods consist in the exchange reaction between catalyst ligands and suitable reactive groups on the surface under formation of covalently bonded Ru species. These methods require appropriate supports having the surface modified with specially constructed linker molecules. This modification is usually connected with intensive synthetic work. Therefore, the possibility of easy immobilization of Ru-alkylidene complexes by simple interaction with support is very challenging. Recently, Hoveyda–Grubbs type catalyst **1a** (Fig. 1) was successfully immobilized on silica surface without any linkers or other surface modifications [11]. The hybrid catalysts prepared by immobilization of **1a** exhibited high activity in ring opening metathesis polymerization (ROMP) of cyclooctene in hexane and in several ring closing metathesis (RCM) reactions. Very low Ru leaching was observed and the possibility of catalyst reusing was reported. In our previous publication [12] we reported on immobilization of the commercially available catalyst **1b** (Zhan catalyst-1B) (Fig. 1) on mesoporous molecular sieves MCM-41 and SBA-15 by direct interaction with molecular sieve surface. The hybrid catalysts prepared exhibited a high catalytic activity in several types of olefin metathesis reactions. Very negligible leaching was found for RCM of 1,7-octadiene in cyclohexane (0.04% of starting Ru content in catalyst), however, for polar solvent the leaching was considerably higher. On the basis of spectroscopic results we concluded that the catalyst was most probably immobilized by non-covalent interactions (physisorption and/or hydrogen bonds).

Mesoporous molecular sieves are characterized by high surface areas, large pore volumes and narrow distributions of pore size [13]. Based on that they are often used as supports for advanced catalysts including metathesis ones [4,14–20]. On the contrary to the conventional type of silica with broad pore size distribution and high

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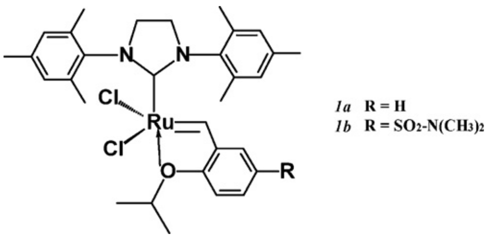


Fig. 1. Hoveyda–Grubbs type catalysts **1a** and **1b**.

fraction of micropores, mesoporous molecular sieves with pores in mesoporous region can facilitate enhanced diffusion of reactants to the catalytic centers (and products in opposite direction), thus, increasing the reaction rates. Using mesoporous supports with large pores, the immobilized catalysts may overcome their often drawback – the considerable reduction in reaction rates of catalyzed reactions in comparison with the corresponding homogeneous systems.

The aim of this contribution is to report on (i) the immobilization of the complex **1b** by direct interaction with the surface of mesoporous molecular sieves differing in pore size (from 4.0 nm to 11.1 nm) and architecture (hexagonal, cubic) and (ii) the effect of support on hybrid catalyst activity and/or selectivity.

2. Materials and methods

2.1. Materials

The synthesis of MCM-41 (surface area $S_{BET} = 972\,m^2/g$, void volume $V = 1.14\,cm^3/g$, and pore size diameter $D = 4.0\,nm$), SBA-15 ($S_{BET} = 934\,m^2/g$, $V = 0.96\,cm^3/g$, $D = 6.9\,nm$), MCM-48 (surface area $S_{BET} = 756\,m^2/g$, void volume $V = 0.914\,cm^3/g$, and pore size diameter $D = 6.0\,nm$) and SBA-15 with large pores (SBA-15LP, $S_{BET} = 610\,m^2/g$, $V = 1.67\,cm^3/g$, $D = 11.1\,nm$) was carried out according to the literature [21–24], respectively. The conventional silica was purchased from the Merck supplier (surface area $S_{BET} = 559\,m^2/g$, void volume $V = 0.47\,cm^3/g$, and pore size diameter $D = 4.5\,nm$). The particle size (by SEM) ranged from 1 μm to 3 μm for all supports used.

Toluene was dried overnight over anhydrous Na_2SO_4, then distilled with Na and stored over molecular sieves 4A. Cyclohexane was distilled with P_2O_5, then dried with CaH_2 and stored over molecular sieves 4A. Cyclooctene (Aldrich, purity 95%) was refluxed with NaH. 1,7-octadiene (Fluka, purity ≥ 97%), (−)-β-citronellene (Aldrich, purity ≥ 90%), 1,9-decadiene (Aldrich, purity 96%), 1-decene (Fluka, purity 98%) were used after passing through the activated alumina column. The Ru complex **1b** was purchased from Zannan Pharma. Ltd., China.

2.2. Techniques

Textural parameters of molecular sieves were determined from nitrogen adsorption isotherms at −196 °C with a Micromeritics ASAP 2020 instrument. The Ru content was determined by ICP-MS (by Institute of Analytical Chemistry, ICT, Prague). 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. Nonane was used as an internal standard, whenever required. Individual products were identified by GC/MS (ThermoFinnigan, FOCUS DSQ II Single Quadrupole). Size-exclusion chromatography (SEC) measurements were carried out on a Watrex Chromatograph fitted with a differential refractometer Shodex RI 101. A series of two PL-gel columns (mixed-B and mixed-C, Polymer Laboratories Bristol, UK) and tetrahydrofuran (THF) (flow rate 0.7 ml/min) were used. The weight average molecular weight, M_w, and number average molecular weight, M_n, relative to polystyrene standards are reported.

2.3. Catalyst preparation

About 1 g of support was transferred into a Schlenk tube and dried for 3 h at 300 °C in vacuo. After drying, the Schlenk tube was filled with argon. Then, 10–15 mL of toluene and a calculated amount of **1b** was added with stirring at room temperature. After stirring for 30 min, the solid phase turned to green and the supernatant became colorless. Later on, the supernatant was removed by filtration and the solid catalyst washed three times with 10 mL toluene. The catalyst was dried in vacuo at room temperature. Catalyst loadings were calculated from Ru content in supernatants. The catalysts were stored in dried glass tubes sealed under argon atmosphere. They were labeled according to the supports used as **1b**/MCM-41, **1b**/MCM-48, **1b**/SBA-15, and **1b**/SBA-15LP. Immobilization of **1b** on conventional silica Merck was performed similarly and the catalyst prepared was labeled as **1b**/SiO_2.

2.4. Catalytic experiments

All catalytic reactions were carried out in Schlenk tubes under an atmosphere of dry argon in cylohexane. In a typical experiment, citronellene (235 mg, 1.69 mmol) was added to **1b**/SBA-15 (28.6 mg, 2.8 μmol of Ru) in cyclohexane (8.5 mL) at 30 °C with continuous stirring. Samples of the reaction mixture (100 μL) were taken at given time intervals, then the reaction was quenched in the samples with ethyl vinyl ether and samples were analyzed by GC. Catalytic activity was expressed in TOF values at given reaction time t (in min), TOF_t, determined with 10% experimental error. In the ROMP experiments, the catalyst was charged in cylohexane at 13 °C. Then cyclooctene was added. After given time intervals, 1 mL samples were collected and polymerization was quenched with 20 μL of ethyl vinyl ether. The catalyst was separated by centrifugation and supernatant was poured into 5 mL MeOH with 2,6-di-tert-butyl *p*-cresol as an antioxidant. The precipitated polymer was dried in vacuo at 60 °C and polymer yield was determined gravimetrically. The molecular weight was determined by SEC.

3. Results and discussion

3.1. Catalyst preparation

Mesoporous molecular sieves of two different architectures were used as supports: hexagonal, MCM-41 ($D = 4.0\,nm$), SBA-15 ($D = 6.9\,nm$) and SBA-15 LP ($D = 11.1\,nm$), and cubic MCM-48 ($D = 6.0\,nm$). Nitrogen isotherms (Fig. 2) show mesoporous character, regular architecture and uniform pore size of these supports. In addition to it, conventional silica with broad pore size distribution and average pore diameter $D = 4.5\,nm$ was used.

Immobilization of **1b** on these supports was performed by simple mixing of **1b** toluene solution with dried supports at room temperature. It proceeded nearly quantitatively: 87–92% of Ru was transferred from solution to the solid phase. Loading of prepared hybrid catalysts **1b**/MCM-41, **1b**/MCM-48, **1b**/SBA-15, **1b**/SBA-15LP and **1b**/SiO_2 was 0.85 wt.% of Ru for each catalyst.

3.2. Catalyst activity in RCM of 1,7-octadiene

Because the leaching of catalytically active species cannot be excluded in polar solvents [11,12] we confined ourselves to the experiments in cyclohexane. Fig. 3 shows conversion curves for

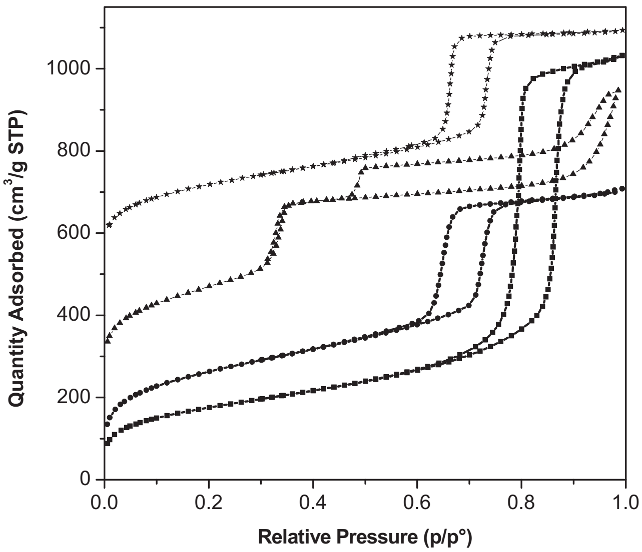


Fig. 2. Adsorption isotherms for SBA-15LP (filled squares), SBA-15 (filled circles), MCM-41 (filled triangles) and MCM-48 (filled stars). For clarity 200 and 500 cm^3/g (STP) was added to the adsorption isotherms of MCM-41 and MCM-48, respectively.

RCM of 1,7-octadiene in cyclohexane (Eq. (1)) over hybrid catalysts differing in pore size: **1b**/MCM-41, **1b**/SBA-15, and **1b**/SBA-15LP.


(1)

The shape of conversion curves is very similar, and the TOF$_{10}$ values approximating the initial activity (TOF$_{10}$ = 28 min^{-1}, 29 min^{-1}, and 26 min^{-1} for **1b**/MCM-41, **1b**/SBA-15, and **1b**/SBA-15LP, respectively) were the same within the frame of experimental error. It indicates that for RCM of 1,7-octadiene, catalyst pore size had no significant effect on the catalyst activity. In all cases, only cyclohexene was observed as the reaction product (selectivity S = 100%).

Fig. 4 shows the filtration test using RCM of 1,7-octadiene with **1b**/SBA-15LP. Filtration test is often used in the examination of heterogeneity in transition metal catalyzed reactions [25].

It helped to distinguish whether catalytic activity can be ascribed to the solid phase or to the transition metal species leached into liquid phase. After 10 min of the reaction, when conversion of 1,7-octadiene reached 45%, a 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 reaction mixture in the original reactor. The analysis showed that in the original reactor, where the liquid phase was in the contact with the solid catalyst, reaction continued till nearly 100% conversion, whereas in the reactor with the liquid phase only the reaction stopped just after separation. It indicates that the metathesis reaction proceeded completely on the surface of the solid catalyst **1b**/SBA-15LP.

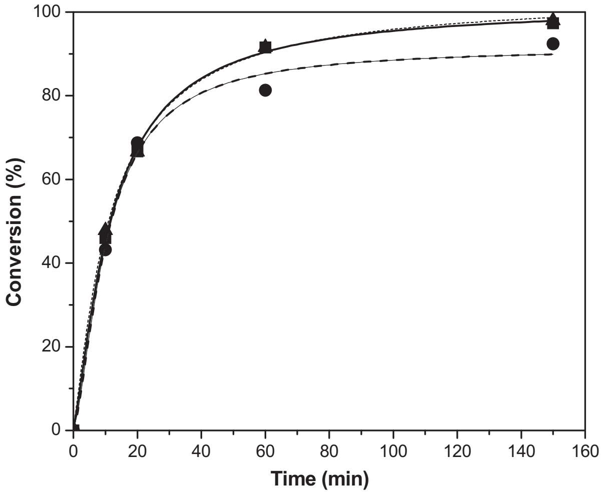
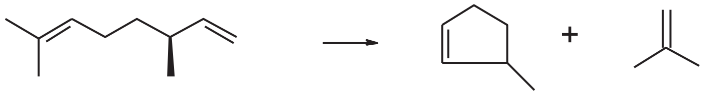


Fig. 3. Conversion curves for RCM of 1,7-octadiene over **1b**/MCM-41 (filled squares), **1b**/SBA-15 (filled triangle), and **1b**/SBA-15LP (filled circles). Cyclohexane, T = 30 °C, molar ratio 1,7-octadiene/Ru = 600, $c^0_{1,7-\text{octadiene}} = 0.2$ mol/L.

Similar filtration test with **1b**/SBA-15 gave the same result [12], which suggests that the leaching of catalytically active species does not depend on the catalyst pore size.

3.3. Catalytic activity in metathesis of bulkier substrates

The effect of the pore size and architecture of the support was studied in RCM of (−)-β-citronellene (Eq. (2)), metathesis of 1-decene (Eq. (3)) and metathesis of 1,9-decadiene (Eq. (4)).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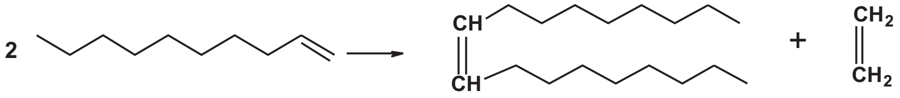

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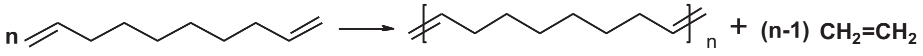


(4)

Conversion curves for RCM of (−)-β-citronellene (Eq. (2)) are displayed in Fig. 5. It is seen that the tested hybrid catalysts exhibited considerably different catalytic activity. The initial activity expressed as TOF$_{15}$ increased in the order **1b**/SiO$_2$ (3.1 min^{-1}) < **1b**/MCM-41 (6.4 min^{-1}) < **1b**/SBA-15 (12.0 min^{-1}) ≈ **1b**/MCM-48 (13.2 min^{-1}) < **1b**/SBA-15LP (20.4 min^{-1}). It corresponds approximately with increasing pore size of supports from conventional silica with important microporous fraction to SBA-15LP with its largest pores of 11.1 nm. This order of activities reflects probably the increasing diffusion rates of citronellene to the catalytically active sites in the pores of individual hybrid catalysts and/or the increasing diffusion rates of products from the catalyst pores. No significant difference in the activity was found for **1b**/SBA-15 and **1b**/MCM-48 suggesting the difference in support architecture (hexagonal vs. cubic) does not play an essential role in this reaction. The catalytic activity of **1b** used as a homogeneous catalyst (TOF$_5$ = 91 min^{-1}) was nearly 30 times higher than the activity of **1b**/SiO$_2$ but only 4.5 times higher than the activity of **1b**/SBA-15LP. It demonstrates the advantage of catalysts immobilized on mesoporous molecular sieves with large pores. With all catalysts only methylcyclopentene and isobutene were found as products (S = 100%).

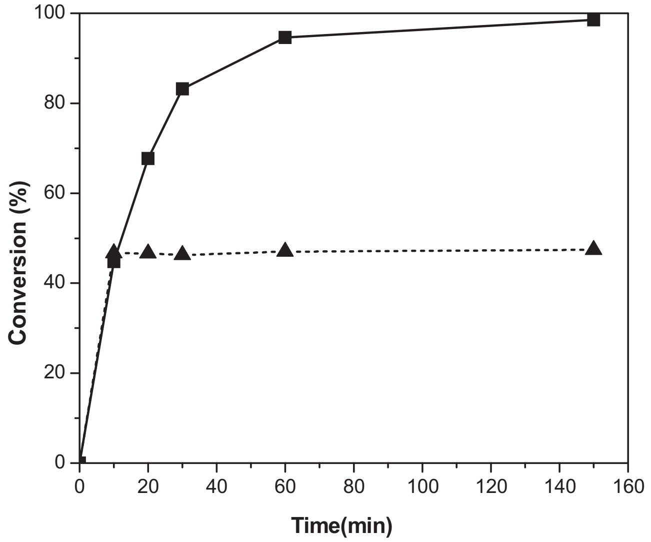


Fig. 4. Filtration experiment for RCM of 1,7-octadiene with **1b**/SBA-15LP. Liquid phase in contact with solid catalyst (filled squares), liquid phase after filtration (filled triangles), cyclohexane, $T = 30\,^{\circ}C$, molar ratio 1,7-octadiene/Ru = 600, $c^0_{1,7-\text{octadiene}} = 0.2$ mol/L.

The conversion curves for 1-decene metathesis (Eq. (3)), (Fig. 6) show the similar dependence of the catalyst activity on the pore size. The TOF_{10} values increased in the order of increasing support pore size: **1b**/SiO_2 (4.9 min^{-1}) < **1b**/MCM-41 (9.0 min^{-1}) < **1b**/MCM-48 (11.4 min^{-1}) ≈ **1b**/SBA-15 (12.0 min^{-1}) < **1b**/SBA-15 LP (16.2 min^{-1}). For the homogeneous reaction with **1b** $TOF_5 = 56$ min^{-1} was found. So **1b** immobilization on SiO_2 led to more than tenfold decrease in the catalytic activity, however, in the case of SBA-15LP this decrease was only 3.5-fold. Again, the positive effect of pore size of support is clearly seen.

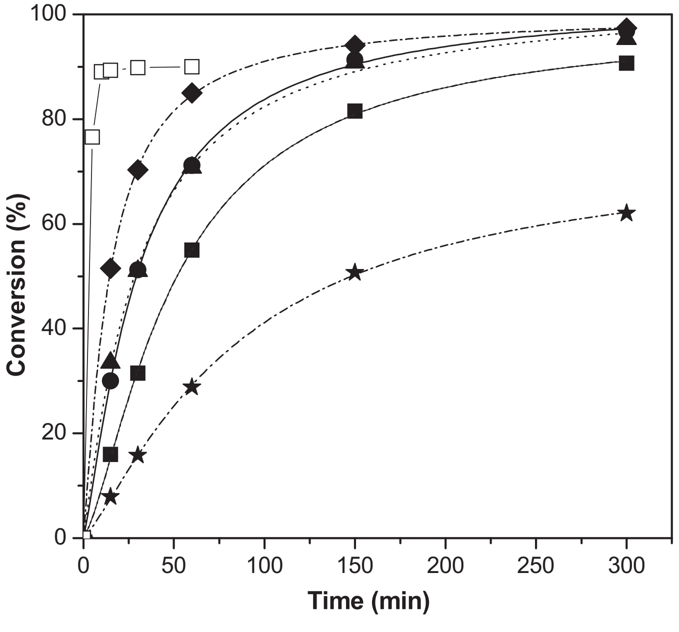


Fig. 5. Conversion curves for RCM of (−)-β-citronellene with **1b** (open squares), **1b**/SiO_2 (filled stars), **1b**/MCM-41 (filled squares), **1b**/MCM-48 (filled triangles), **1b**/SBA-15 (filled circles), **1b**/SBA-15LP (filled diamonds). Cyclohexane, $T = 30\,^{\circ}C$, molar ratio citronellene/Ru = 600, $c^0_{\text{citronellene}} = 0.2$ mol/L.

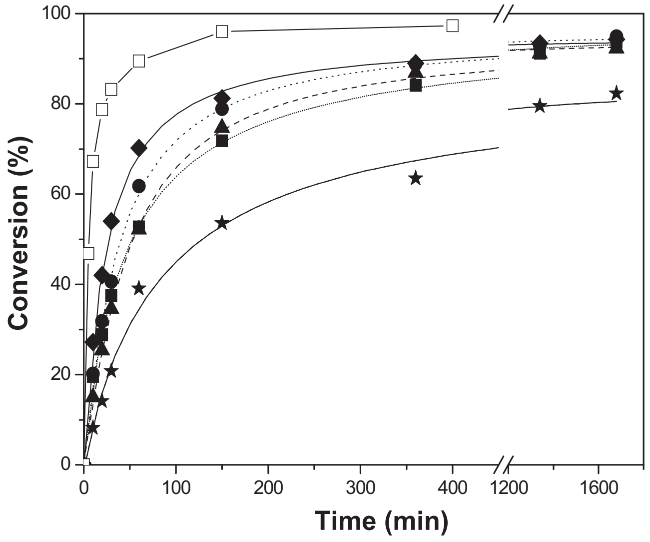


Fig. 6. Conversion curves for 1-decene metathesis with **1b** (open squares), **1b**/SiO_2 (filled stars), **1b**/MCM-41 (filled squares), **1b**/MCM-48 (filled triangles), **1b**/SBA-15 (filled circles), **1b**/SBA-15LP (filled diamonds). Cyclohexane, $T = 60\,^{\circ}C$, molar ratio 1-decene/Ru = 600, $c^0_{\text{1-decene}} = 0.6$ mol/L.

The immobilization has considerable effect on the selectivity (Fig. 7). The decrease in the selectivity is due to the double bond shift isomerization followed by the cross-metathesis [26]. In addition to the main metathesis product, 9-octadecene, homologues with shorter chain C_{17}–C_{11} were formed. The selectivity S was then calculated using formula $S = 100\, n_P/(n_P + \sum n_i)$, where n_P, n_i are molar amounts of the main metathesis product and the cross-metathesis products C_{17}–C_{11}, respectively. Fig. 7 shows that all hybrid catalysts were less selective than the corresponding homogeneous system up to 90% conversion. It suggests the higher extent of 1-decene isomerization in the case of hybrid catalysts in comparison with homogeneous systems. The supports themselves can hardly be denoted as efficient catalysts for double bond shift isomerization, because (i) mesoporous molecular

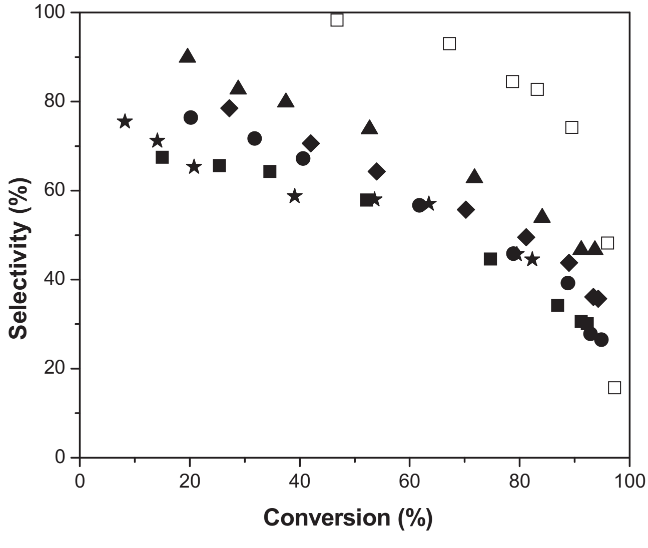


Fig. 7. Selectivity for 1-decene metathesis with **1b** (open squares), **1b**/SiO_2 (filled stars), **1b**/MCM-41 (filled squares), **1b**/MCM-48 (filled triangles), **1b**/SBA-15 (filled circles), **1b**/SBA-15LP (filled diamonds). Cyclohexane, $T = 60\,^{\circ}C$, molar ratio 1-decene/Ru = 600, $c^0_{\text{1-decene}} = 0.6$ mol/L.

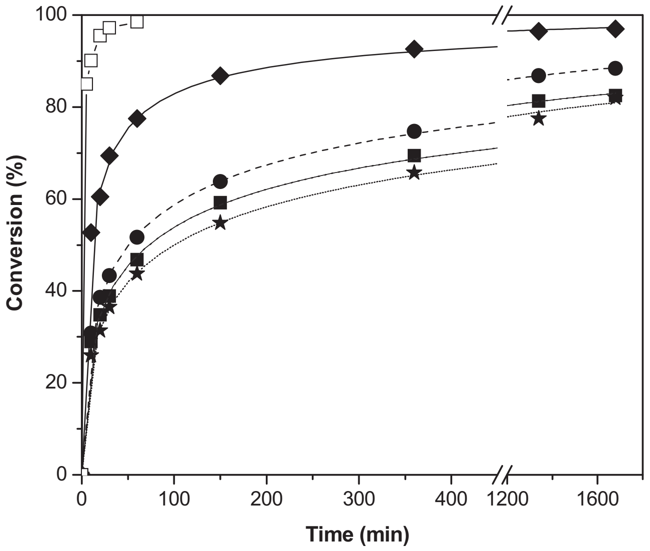


Fig. 8. Conversion curves for 1,9-decadiene metathesis with **1b** (open squares), **1b**/SiO_2 (filled stars), **1b**/MCM-41 (filled squares), **1b**/SBA-15 (filled circles), **1b**/SBA-15LP (filled diamonds). Cyclohexane, $T = 60\,°C$, molar ratio 1-decene/Ru = 600, $c^0_{1,9\text{-decadiene}} = 0.6\,\text{mol/L}$.

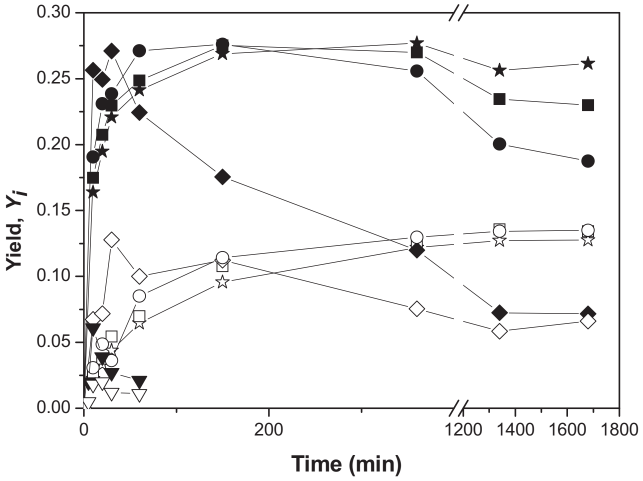


Fig. 9. Yields (Y_i) of ADMET dimers (filled symbols) and trimers (open symbols) in ADMET of 1,9-decadiene with **1b** (down triangles), **1b**/SiO_2 (filled stars), **1b**/MCM-41 (filled squares), **1b**/SBA-15 (filled circles), **1b**/SBA-15LP (filled diamonds). Cyclohexane, $T = 60\,°C$, molar ratio 1-decene/Ru = 600, $c^0_{1,9\text{-decadiene}} = 0.6\,\text{mol/L}$.

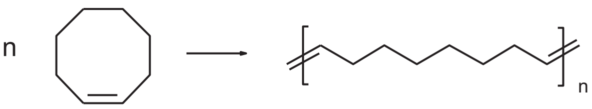
sieves used are non-acidic, and (ii) no 1-decene isomerization was observed in blank experiment (466 μL 1-decene, 41 mg SBA-15, 4.2 mL cyclohexane, 60 °C). Double bond shift isomerization during metathesis with homogeneous Ru catalysts is usually assigned to the ruthenium hydrides formed during catalyst decomposition [27,28]. Therefore, we suggest that the drop in selectivity after catalyst immobilization may be due to the increased rate of Ru hydrides formation and/or to the increased reactivity of these hydride species in 1-decene isomerization in the course of metathesis over hybrid catalysts. The differences in the Ru hydrides formation rates and/or in their reactivity may be also responsible for different selectivity of individual hybrid catalysts: the highest selectivity was found for **1b**/MCM-48, the lowest one for **1b**/MCM-41 and **1b**/SiO_2.

1,9-Decadiene metathesis, an example of acyclic diene metathesis (ADMET), proceeds under formation of so called ADMET oligomers and ethylene (Eq.(4)). Conversion curves (1,9-decadiene consumption vs. time) are shown in Fig. 8. Similarly to the previous reaction, TOF_{10} values increased in the order **1b**/SiO_2 (15.6 min^{-1}) < **1b**/MCM-41 (17.5 min^{-1}) ≈ **1b**/SBA-15 (18.1 min^{-1}) < **1b**/SBA-15 LP (31.6 min^{-1}). Hence, the initial activity of **1b** as a homogeneous catalyst ($TOF_5 = 102\,min^{-1}$) was 6.5 times and 3.3 times higher in comparison with that of **1b**/SiO_2 and **1b**/SBA-15LP, respectively.

Formation of ADMET oligomers was observed in all cases. The dependence of selectivity to the individual oligomers on catalyst pore size can be expected [29]. Fig. 9 shows yields of octadeca-1,9,17-triene (ADMET dimer) and hexacosa-1,9,17,25-tetraene (ADMET trimer) plotted against reaction time. The yield was calculated on the bases of GC analysis using the formula $Y_i = q_i n_i / n_s$, where n_i is the molar amount of an individual oligomer, n_s is the molar amount of 1,9-decadiene consumed, and q_i is a stoichiometric coefficient ($q_i = 2$, 3 for dimer and trimer, respectively). It should be noted that the positions of double bonds in these compounds were supposed relating to the mechanism of olefin metathesis reaction. It is seen from Fig. 9 that very small amounts of ADMET dimers and trimers were found in the beginning of the reaction with **1b**. Both these low oligomers were consumed rapidly giving rise to higher oligomers in agreement with ADMET mechanism. In the case of immobilized catalysts, ADMET dimers and trimers were found in considerably higher amounts and they persisted in the reaction mixture till the end of the experiment. For the catalyst with the largest pores (**1b**/SBA-15LP), their concentrations passed through a sharp maximum, however, for other hybrid catalysts (**1b**/SiO_2, **1b**/MCM-41, and **1b**/SBA-15) very flat maximum for trimer concentration and continuous increase in dimer concentration were found. It may indicate that in the latter case dimers and trimers once released into liquid phase were not able to re-enter the pores and to take part in consecutive reactions. Thus, changes in dimer and trimer concentrations demonstrate the influence of pore size on the selectivity in this ADMET reaction. However, the main reaction products were the higher ADMET oligomers in all cases. For example, reaction catalyzed by **1b** delivered oligomeric product of $M_w = 3500$ (SEC) in 55% isolated yield. For **1b**/SBA-15, product of bimodal molecular weight distribution with maxima at molecular weights 1300 and 630 was found.

3.4. Catalyst activity in ROMP of cyclooctene

ROMP of cyclooctene (Eq. (5)) with silica immobilized **1a** was reported in Ref. [11]. High conversions and TOF_{10} values up to 60 min^{-1} were reported. However, no product characterization was given. Therefore, we concentrated on the effect of catalyst support on the yield and molecular weight characteristics of polymers formed.



(5)

It is seen from Fig. 10 that the initial rate of polymer formation increased in the order: **1b**/SiO_2 < **1b**/MCM-41 ≈ **1b**/SBA-15 < **1b**/SBA-15LP, which may reflect the accessibility of catalytic centers located in the pores of different size. For **1b**/SiO_2, the polymerization stopped after 15 min of the reaction while for catalysts based on mesoporous supports the polymerization proceeded further till 1 h when the conversions between 70 and 80% were reached. The early ceasing of polymerization for **1b**/SiO_2 may be due to the blocking of narrow pores by polymers preventing the access to the catalyst centers. Similarly low polymer yields have already been observed for ROMP over silica immobilized Ru complexes [17,30].

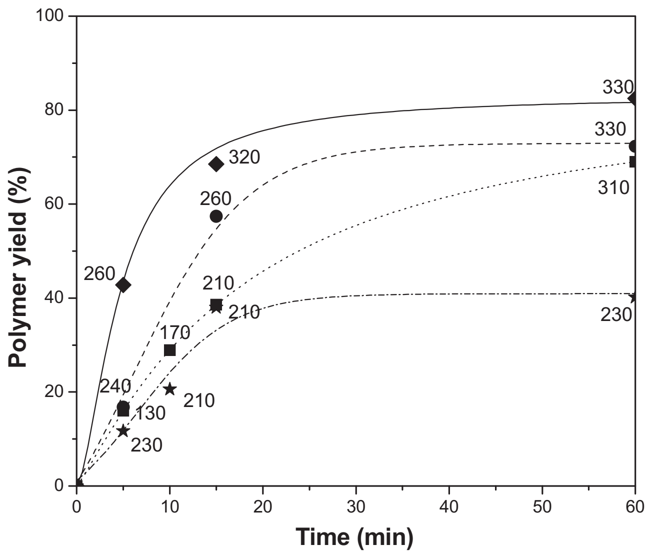


Fig. 10. ROMP of cyclooctene with **1b**/SiO_2 (filled stars), **1b**/MCM-41 (filled squares), **1b**/SBA-15 (filled circles), **1b**/SBA-15LP (filled diamonds). Cyclohexane, $T = 13\,^{\circ}C$, molar ratio cyclooctene/Ru = 500, $c^0_{\text{cyclooctene}} = 0.6$ mol/L, number at individual experimental points give M_w of polymer in thousands.

For all polymers prepared, SEC revealed bimodal distribution of molecular weight consisting of a high molecular weight peak (75% of area) and a low molecular weight peak (oligomers of M_w about 5000, 25% of area). M_w values calculated from high molecular weight peaks of individual polymers (in thousands) are given in Fig. 10. Dispersity index, $I = M_w/M_n$, was about 2.0 for all high molecular weight polymer fraction. For **1b**/MCM-41, **1b**/SBA-15, and **1b**/SBA-15LP systematic increase in the polymer molecular weight in the course of the polymerization was clearly observed. However, for **1b**/SiO_2 polymer of $M_w = 230{,}000$ was formed in 5 min, and no increase in the M_w was observed later. It may be caused by the chain transfer and/or polymer degradation. After 1 h reaction, all catalysts based on mesoporous supports delivered polymers of M_w slightly higher than 300,000, which is higher molecular weight in comparison with polymer prepared with **1b**/SiO_2.

IR spectra confirmed that the structure of all polymers was in accord with the ROMP mechanism (Eq.(5)). The trans/cis double bond ratio calculated from IR spectra (using empirical equation derived previously [17] trans/cis = 1.89 A_{966}/A_{720}, where A_{966} and A_{720} are the areas of IR absorption bands at 966 cm^{-1} and 720 cm^{-1}, respectively) was in the range from 3.8 to 6.2. No systematic changes of trans/cis ratio were observed.

4. Conclusions

Hybrid olefin metathesis catalysts were prepared by immobilization of Hoveyda–Grubbs type catalyst **1b** (Zhan catalyst-1B) by direct interaction with the surface of mesoporous molecular sieves MCM-41, MCM-48, SBA-15 and SBA-15LP differing in the pore size (from 4.0 to 11.1 nm) and architecture (hexagonal, cubic), and also of conventional silica for a comparison. The immobilization proceeded nearly quantitatively and catalysts with 0.85 wt.% of Ru were obtained. Although non-covalent interactions between support surface and Ru species are assumed, the catalytically active species seemed to be bound firmly to the surface (at least in cyclohexane we used as a solvent) and the filtration test carried out for RCM of 1,7-octadiene did not indicate the leaching of catalytically active species into liquid phase.

Significant effect of the support pore size on hybrid catalyst activity was found in RCM of (−)-β-citronellene, metathesis of 1-decene, ADMET of 1,9-decadiene, and in ROMP of cyclooctene. For reaction of (−)-β-citronellene, 1-decene, and 1,9-decadiene, the initial TOF values were found to increase with increasing pore size, however, no significant effect of changing hexagonal support for cubic one on TOF was found. The activity of hybrid catalysts based on mesoporous molecular sieves was higher in comparison with that of conventional silica based catalyst, in all reactions studied. The initial TOF for catalyst supported on SBA-15LP (pore diameter 11.1 nm) was only 3.3–4.5 times lower in comparison with the initial TOF of **1b** used as a homogeneous catalyst. In the case of ROMP, high molecular weight polymers (M_w about 300,000) in high yield (70–80%) were obtained for hybrid catalyst based on mesoporous supports. However, for conventional silica based catalyst the polymerization stopped prematurely and only 40% polymer yield was obtained. All these results demonstrate the advantage of mesoporous molecular sieves as supports for olefin metathesis catalysts and the usefulness of the employment of supports with large mesopores.

The effect of the support on the selectivity was found in 1-decene metathesis (the difference in the amounts of side products formed by olefin double bond shift followed by cross-metathesis) and in ADMET of 1,9-decadiene (different populations of ADMET dimers and trimers in reaction mixture).

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