



RuCl₂(*p*-cymene)(PCy₃) immobilized on mesoporous molecular sieves as catalyst for ROMP of norbornene and its derivatives

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ABSTRACT

New heterogeneous catalysts for ring opening metathesis polymerization (ROMP) have been prepared by immobilization of RuCl₂(*p*-cymene)(PCy₃) (Cy = cyclohexyl) on silica and siliceous mesoporous molecular sieves SBA-15 and MCM-41. Activity of these catalysts was investigated in ROMP of norbornene (NBE) and its derivatives (dicyclopentadiene, 5-norbornene-2-yl acetate). High molecular weight polymers (*M_w* up to 400 000) were prepared in yields up to 80% using catalysts based on mesoporous sieves. In contrast, with catalyst based on conventional silica the yield did not exceed 28% (ROMP of NBE). Filtration test proved that the catalytic activity was bound to the solid phase. Catalysts could be easily separated from the reaction mixture in contrast to the corresponding homogeneous system. Therefore, polymers with reduced amounts of catalyst residues were obtained.

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1. Introduction

Ring opening metathesis polymerization (ROMP), a member of olefin metathesis reaction family, represents an indispensable tool for the preparation of high molecular weight polymers of various practical applications [1]. Various Ta, W, Mo and Ru compounds were used as catalysts for this reaction [2]. Systems based on tungsten and molybdenum chlorides, oxochlorides and aryloxocomplexes belong to the very active and widely used catalysts, applied also in large scale polymerizations [3–5]. Well-defined Mo alkylidenes (Schrock catalysts) combine high catalytic activity with a possibility to control the polymer molecular weight and polymer microstructure in some extent [6,7]. The main advantage of Ru based catalysts is their enhanced stability under ambient conditions and tolerance to the wide range of polar groups [8]. Therefore, modern well-defined Ru-alkylidene complexes (Grubbs catalysts) became preferred catalysts for a great variety of metathesis reaction, including ROMP [9]. However, these catalysts are rather expensive and alternative catalyst precursors that are air stable and easily accessible have been developed. These precursors are represented by [RuCl₂(*p*-cymene)]₂ and related complexes that can be easily prepared from the parent dimer [10–17]. The active catalytic centres, i.e. alkylidene complexes, are formed *in situ* in the reaction systems using diazocompounds [10–12], alkynes [13,14], and/or

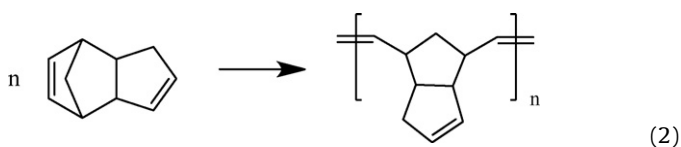
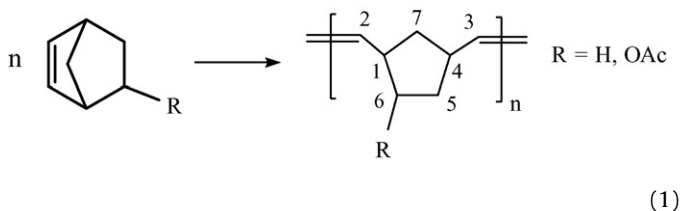
via system irradiation [15–17]. [RuCl₂(*p*-cymene)]₂ itself is active for polymerization of norbornene (NBE) when activated by addition of catalytic amounts of (trimethylsilyl)diazomethane (TMSD) [10]. Mononuclear phosphine complexes RuCl₂(*p*-cymene)(PR₃), which can be prepared by a direct reaction of [RuCl₂(*p*-cymene)]₂ with PR₃ (R = alkyl, cycloalkyl, aryl) [10] are active in ROMP of NBE as well as unstrained cycloolefins [10,11]. In the case of NBE, the Ru-alkylidene is formed without participation of TMSD by the reaction of RuCl₂(*p*-cymene)(PR₃) with the monomer (a suggestion of the mechanism is given in Ref. [18]). In the case of unstrained cycloolefins the addition of TMSD is necessary. Among the series of various PR₃ phosphines, PCy₃ (Cy = cyclohexyl) was found to generate the most active precatalyst for ROMP.

Mesoporous molecular sieves are siliceous and/or aluminous materials with well-defined regular architecture, large surface area, large void volume and narrow pore size distribution of mesopores [19–21]. They are used as excellent supports for different catalysts [22–27]. Immobilization of soluble metathesis catalysts (including Schrock and Grubbs alkylidenes) on siliceous sieves MCM-41 and SBA-15 provides heterogeneous metathesis catalysts with high activity and selectivity and low metal leaching. These catalysts are easily separable from the reaction mixture by simple filtration or centrifugation delivering a product free of catalyst residues [28–32]. The mesoporous structure of these catalysts ensures not only an easy access to the catalytic centres but also a facile release of bulky products from the catalyst pores. Therefore, these catalysts can be used also in polymerization reactions. Recently, we have referred about the immobilization of [RuCl₂(*p*-cymene)]₂ on

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SBA-15 by direct reaction of the complex with the support surface [33]. Heterogeneous catalyst prepared exhibited, after its activation with TMSD, high activity in ROMP of NBE providing a high molecular weight polymer (PNBE) in high yields. PNBE formed was easily separated from the catalyst and its contamination with Ru residues was significantly reduced in comparison with the contamination of PNBE prepared under the same conditions with $[\text{RuCl}_2(p\text{-cymene})]_2$ used as a homogeneous catalyst.

In this contribution we describe the immobilization of $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$ on mesoporous molecular sieves MCM-41 and SBA-15. The immobilized complexes were tested as catalysts for ROMP of NBE, 5-norbornene-2-yl acetate (NBEAc) (Eq. (1)) and dicyclopentadiene (Eq. (2)):



2. Experimental

2.1. Material

Mesoporous molecular sieves MCM-41 and SBA-15 were prepared according to the procedure described elsewhere [34]. Their textural characteristics determined from nitrogen adsorption isotherms were the following (MCM-41 and SBA-15, respectively): surface area $S_{\text{BET}} = 1032$ and $829 \text{ m}^2/\text{g}$, average pore diameter $d = 3.7$ and 6.6 nm , volume of pores $V = 0.81$ and $1.18 \text{ cm}^3/\text{g}$. Silica gel 40, Merck (surface area $S_{\text{BET}} = 559 \text{ m}^2/\text{g}$, average pore diameter $d = 4.5 \text{ nm}$, broad distribution of pore size, volume of pores $V = 0.473 \text{ cm}^3/\text{g}$), was taken as a conventional silica support with broad pore distribution for comparison.

Toluene (Lach-Ner, Czech Rep.) was dried overnight using anhydrous Na_2SO_4 , distilled from Na and stored over molecular sieves 4A. Dichloromethane (Lach-Ner) was dried overnight by anhydrous CaCl_2 , then distilled from P_2O_5 and stored over molecular sieves 4A. DCPD (Chemical Plants in Litvínov, Czech Rep.) was stripped by nitrogen. Norbornene (Aldrich, purity 99%), 5-norbornene-2-yl acetate (Aldrich, 98%, mixture endo and exo), $[\text{RuCl}_2(p\text{-cymene})]_2$ (Sigma–Aldrich) and TMSD (Sigma–Aldrich, 2.0 M solution in hexanes) were used as received. $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$ was kindly provided by A. Demonceau (University of Liege).

2.2. Catalysts preparation

Weighted amount of support predried for 3 h at 300°C was placed into a Schlenk tube filled with Ar. Then CH_2Cl_2 (3–5 volume excess) and calculated amount of $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$ were added under stirring at room temperature. After 1 h of stirring, the yellow catalyst was let to settle down. Then, the supernatant of only very slightly yellow colour was removed; the catalyst was washed out three times with CH_2Cl_2 and finally dried in vacuo at room temperature. The catalysts (denoted as $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$, $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$

and $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{silica}$, respectively) with Ru loading of 1 wt.% were stored under argon atmosphere.

2.3. Polymerization experiments

Polymerizations were performed in Schlenk tubes under Ar atmosphere in toluene. In a typical experiment, NBE (94 mg, 1 mmol) was added to $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$ (45 mg, $4.5 \mu\text{mol}$ Ru) in toluene (9 ml) at 40°C under stirring. 1 ml samples of the reaction mixture were taken at given reaction times and polymerization was quenched with $10 \mu\text{l}$ of ethyl vinyl ether. Catalyst was separated by centrifugation and the supernatant was poured into 3 ml of methanol 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 NBE conversion was determined by GC using ethyl vinyl ether as an internal standard. The polymerization experiment was repeated 3 times and the absolute error in the determination of conversion was about 2%.

2.4. Techniques

Textural parameters of molecular sieves were determined from nitrogen adsorption isotherms at -196°C with a Micromeritics ASAP 2020 instrument. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra of polymers were recorded on a Varian Mercury 300 spectrometer in CDCl_3 at 25°C . Chemical shifts (δ , ppm) are given relative to solvent signals. $\{^1\text{H}\}^{13}\text{C}$ CP/MAS NMR spectra of solid catalyst were recorded on a Bruker Avance 500 MHz (11.7 T) Wide Bore spectrometer using 4 mm o.d. ZrO_2 rotors with a rotation speed of 12 kHz using 50% ramp cross polarization (CP) pulse sequence. The ^{13}C chemical shifts were referenced to glycine. UV–vis spectra of catalysts were recorded using a Perkin-Elmer Lambda 950 spectrometer. A spectralon integration sphere was applied to collect diffuse reflectance spectra of powder samples. Spectralon served also as a reference. Catalyst samples were placed in a quartz cuvette under Ar atmosphere. The 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 $K\alpha$ radiation was used for electron excitation. The spectra were recorded at room temperature. The Si 2p, O 1s, Cl 2p, C 1s and Ru 3d photoelectrons were measured. Sample charging was corrected using the Si 2p peak at 103.4 eV as internal standard. For overlapping C 1s and Ru 3d lines, the contributions of individual components were determined by curve fitting.

A high-resolution gas chromatography Agilent 6890 with DB-5 column (length: 50 m, inner diameter: $320 \mu\text{m}$, stationary phase thickness: $1 \mu\text{m}$) was used for the determination of the NBE content in the reaction mixture. Size-exclusion chromatography (SEC) measurements of the polymers 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 $0.7 \text{ ml}/\text{min}$) were used. Weight average molecular weight, M_w , and number average molecular weight, M_n , relative to polystyrene standards are reported. Content of Ru was determined by ICP-MS (by Institute of Analytical Chemistry, ICT, Prague).

3. Results and discussion

3.1. Catalyst preparation and characterization

The immobilization of $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$ on all supports tested proceeded very easily at room temperature. According to the analysis of supernatants and washing solutions about 95% of

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