

# RuCl<sub>2</sub>(*p*-cymene)(PCy<sub>3</sub>) 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 RuCl<sub>2</sub>(*p*-cymene)(PCy<sub>3</sub>) (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<sub>w</sub>* 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 [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> 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

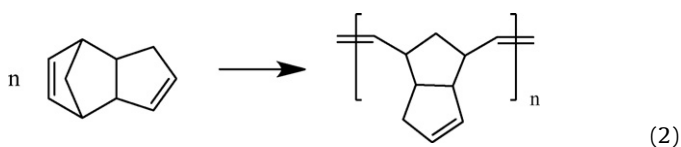
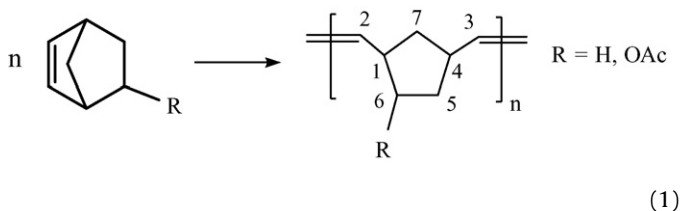
via system irradiation [15–17]. [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> itself is active for polymerization of norbornene (NBE) when activated by addition of catalytic amounts of (trimethylsilyl)diazomethane (TMSD) [10]. Mononuclear phosphine complexes RuCl<sub>2</sub>(*p*-cymene)(PR<sub>3</sub>), which can be prepared by a direct reaction of [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> with PR<sub>3</sub> (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 RuCl<sub>2</sub>(*p*-cymene)(PR<sub>3</sub>) 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 PR<sub>3</sub> phosphines, PCy<sub>3</sub> (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 [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> 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  $6.6 \text{ nm}$ , 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  $\text{Na}_2\text{SO}_4$ , distilled from Na and stored over molecular sieves 4A. Dichloromethane (Lach-Ner) was dried overnight by anhydrous  $\text{CaCl}_2$ , then distilled from  $\text{P}_2\text{O}_5$  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  $300^\circ\text{C}$  was placed into a Schlenk tube filled with Ar. Then  $\text{CH}_2\text{Cl}_2$  (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  $\text{CH}_2\text{Cl}_2$  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  $40^\circ\text{C}$  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  $60^\circ\text{C}$  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  $-196^\circ\text{C}$  with a Micromeritics ASAP 2020 instrument.  $^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  (75 MHz) NMR spectra of polymers were recorded on a Varian Mercury 300 spectrometer in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ . Chemical shifts ( $\delta$ , 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.  $\text{ZrO}_2$  rotors with a rotation speed of 12 kHz using 50% ramp cross polarization (CP) pulse sequence. The  $^{13}\text{C}$  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

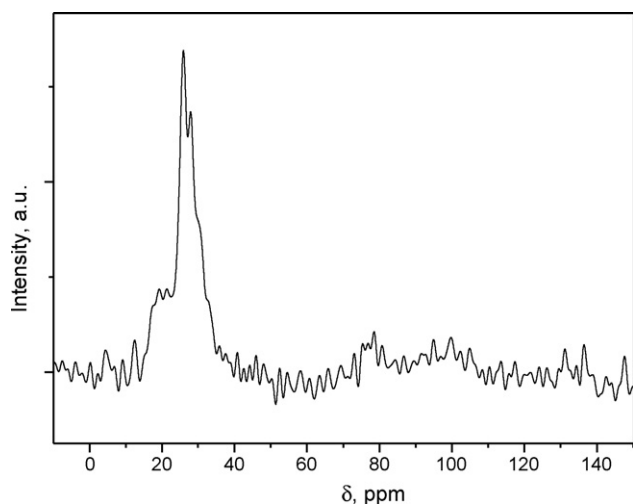


Fig. 1.  $\{^1\text{H}\}^{13}\text{C}$  CP MAS NMR spectrum of  $\text{RuCl}_2(p\text{-cymene})\text{PCy}_3/\text{SBA-15}$ .

$\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  submitted was attached to the support and catalysts of 1 wt.% of Ru were prepared.

Fig. 1 shows  $\{^1\text{H}\}^{13}\text{C}$  CP MAS NMR spectrum of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$ . Using signals of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  in  $\text{CDCl}_3$  [10] the signal assignment is the following ( $\delta$ , ppm): 20 ( $\text{CH}_3 + \text{CH}(\text{CH}_3)_2$ ); 26 (cyclohexyl  $\text{CH}_2$ ); 28 ( $\text{CH}(\text{CH}_3)_2$ ); 30sh (cyclohexyl  $\text{CH}_2$ ); 33sh (cyclohexyl  $\text{CH}$ ), 80 (arom.), 99 (arom.). The spectrum clearly shows that both *p*-cymene and tricyclohexylphosphine ligands are present in the immobilized complex. The presence of tricyclohexylphosphine ligand is further supported by  $^{31}\text{P}$  MAS NMR showing a single broad signal at 27 ppm.

Fig. 2 shows UV–vis spectra of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  and  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$ .  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  in  $\text{CH}_2\text{Cl}_2$  exhibits a MLCT band at 367 nm (which may be ascribed to the Ru ( $d$ )–Ph ( $\pi$ ) transition [35]) and a shoulder at about 490 nm. Diffuse reflectance spectrum of  $\text{RuCl}_2(p\text{-cymene})\text{PCy}_3/\text{SBA-15}$  exhibits absorption bands at 345 and 422 nm indicating that the coordination sphere of Ru atom is affected as a result of immobilization.

Surface stoichiometry determined from photoelectron spectra of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$  was  $\text{Si}_{1.00}\text{O}_{2.06}\text{Cl}_{0.008}\text{Ru}_{0.008}\text{C}_{0.18}$ . The observed surface Ru:Cl atomic concentration ratio is consistent with the notion that one chloro ligand is liberated during immobilization. For binding energy of Ru  $3d_{5/2}$  electrons values 280.8 and 278.0 eV were found (the ratio of corresponding peak areas was approximately 1.5). The former

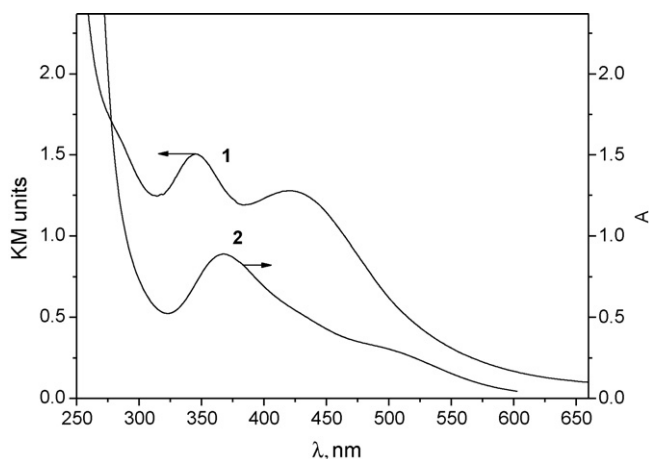


Fig. 2. UV–vis spectra of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  (1) and  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  in  $\text{CH}_2\text{Cl}_2$  ( $c = 0.004$  mol/l,  $l = 0.2$  cm) (2).

value is by 0.6 eV lower than the value which we obtained for the Ru  $3d_{5/2}$  binding energy in the neat  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  complex (281.4 eV). The latter value is unusually low for Ru complexes, which might be due to the differential charging of the sample surface during spectra measurement [36].

The more detailed description of the mode of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  immobilization on MCM-41 and SBA-15 is not possible on the basis of the results obtained so far. The observed atomic ratio Ru:Cl=1 might suggest the reaction with surface OH groups occurs under formation of Si–O–Ru bond. The binding energy 280.8 eV does not contradict to it. However, this bond is known to be formed in basic environment or from alkali metal silanates [37,38] and we have not obtained any direct evidence for the presence of this bond in our catalysts. Recently, van Berlo et al. [39] described immobilization of Hoveyda–Grubbs catalyst on silica. On the basis of FT-IR and  $^{29}\text{Si}$  MAS NMR they suggested a direct chemical interaction of Ru complex and silanol groups of the surface. However, the loading of our catalysts is too low to detect significant changes in intensity of OH signal in FT-IR and appropriate changes in  $^{29}\text{Si}$  MAS NMR (approximately 2% of OH groups present on the surface could interact with Ru atoms). The attempt to prepare catalyst of higher loading using procedure described above failed.

### 3.2. ROMP and polymer characteristics

Fig. 3 shows the polymer yield vs. reaction time curves for ROMP of NBE with the catalyst prepared by immobilization of  $[\text{RuCl}_2(p\text{-cymene})]_2$  on SBA-15 ( $[\text{RuCl}_2(p\text{-cymene})]_2/\text{SBA-15}$ ) [33] and with the catalyst  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$ . The numbers at individual experimental points indicate values of polymer weight average molecular weight  $M_w$ . Whereas  $[\text{RuCl}_2(p\text{-cymene})]_2/\text{SBA-15}$  had to be combined with TMSD (TMSD/Ru molar ratio = 10) to obtain good activity,  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  was active without any cocatalyst. In the former case, where the catalytically active species (Ru-alkylidenes) are formed by the reaction with TMSD, the initial polymerization rate was high and a polymer of very high molecular weight and high polydispersity (polydispersity index  $I_n = 9$ ) was formed just at the beginning of the reaction. In the further reaction course the molecular weight of polymer continually decreased to less than half the starting value and  $I_n$  was continually reduced to 5.3. It indicates the formation of a small amount of very active species at the early stages of the

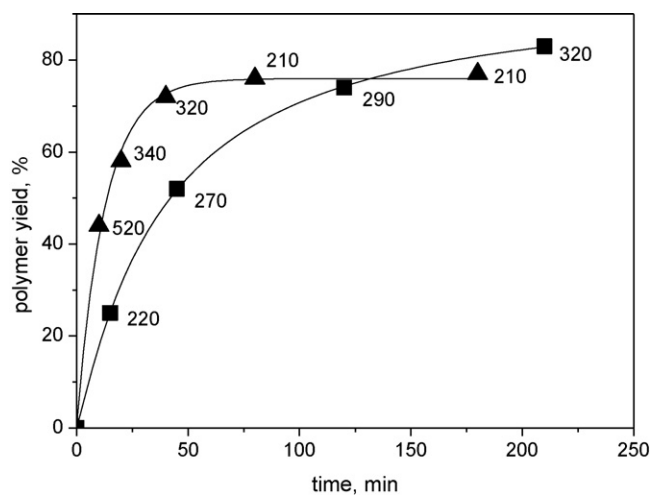
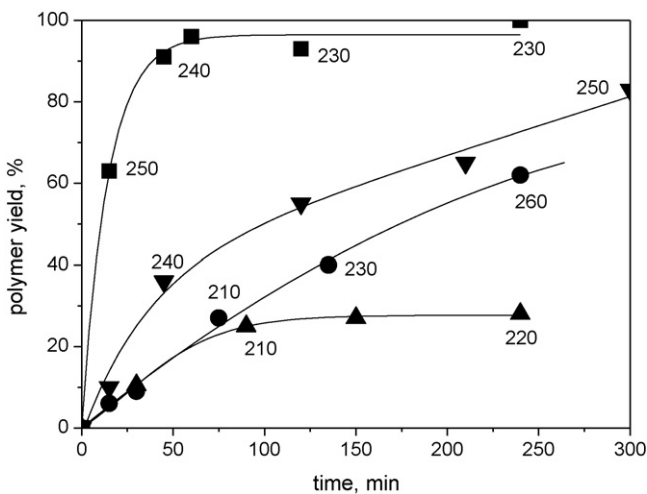


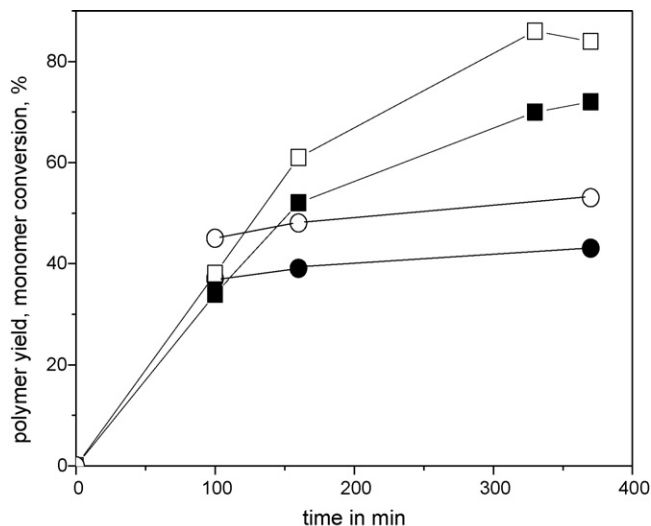
Fig. 3. ROMP of NBE with  $[\text{RuCl}_2(p\text{-cymene})]_2/\text{SBA-15} + \text{TMSD}$  (triangle) and  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  (square). Toluene,  $t = 60^\circ\text{C}$ , NBE/Ru molar ratio = 220,  $c_0(\text{NBE}) = 11$  mg/ml, numbers at individual experimental points give  $M_w$  of polymer in kDa.



**Fig. 4.** ROMP of NBE with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  (squares),  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$  (down triangle),  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  (circles) and  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{silica}$  (up triangle). Toluene,  $t=40^\circ\text{C}$ , NBE/Ru molar ratio = 220,  $c_{0(\text{NBE})} = 10\text{ mg/ml}$ , numbers at individual experimental points give  $M_w$  of polymer in kDa.

polymerization reaction and an increasing extent of chain transfer reactions and/or polymer degradation in the course of the reaction. On the other hand, with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$ , the initial reaction rate was considerably lower, polymer molecular weight slightly increased with reaction time and  $I_n$  was about 1.8 during the whole polymerization. It suggests that in this case the formation of catalytically active species by the reaction with NBE proceeded more slowly and the extent of the chain transfer and degradation reactions was lower. Thus,  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  provided high molecular weight PNBE of similar  $M_w$  as  $[\text{RuCl}_2(p\text{-cymene})_2/\text{SBA-15}]$  did but of considerably lower polydispersity.

Fig. 4 shows the influence of individual supports on the course of polymerization process. The catalysts prepared by immobilization of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  on MCM-41, SBA-15 and conventional silica were compared with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  used as a homogeneous catalyst. In all cases high molecular weight polymers of similar molecular weights ( $M_w$  between 220 000 and 260 000,  $I_n = 1.7\text{--}2.0$ ) were formed. No systematic changes in molecular weight with reaction time were observed. The development of molecular weight during polymerization (differences in the range of experimental error in most cases and  $I_n$  between 1.7 and 2.0) indicates a similar extent of chain transfer processes and/or polymer degradation for all catalysts tested. Significant differences were found in the initial reaction rates and the polymer yields. For simplicity (Fig. 4), polymer yields are presented only, monomer conversions were the same or up to 20% higher in comparison with the polymer yields. Initial reaction rate can be approximated by turnover frequency  $\text{TOF}_{15} = \text{weight of polymer produced at 15 min}/900 \text{ initial weight of Ru in catalyst}$ .  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  used as a homogeneous catalyst exhibited the highest initial rates ( $\text{TOF}_{15} = 0.146\text{ s}^{-1}$ ) reaching nearly quantitative polymer yield at 1 h. Complex immobilization led to a considerable decrease in the initial reaction rate, which can be explained by monomer diffusion into the catalyst pores. Initial reaction rate with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$  ( $\text{TOF}_{15} = 0.034\text{ s}^{-1}$ ) was repeatedly found significantly higher than that with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  ( $\text{TOF}_{15} = 0.014\text{ s}^{-1}$ ). A tentative explanation could be the microporosity of the walls and/or the wall surface corrugation observed for SBA-15 supports [34,40]. A considerable fraction of Ru species may be placed in these micropores and notches and can be hardly accessible for monomer molecules. In the case of  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{silica}$  the polymerization proceeded with a similar



**Fig. 5.** ROMP of NBE with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$  with partial separation of the liquid phase at 100 min of the reaction. Polymer yield (solid symbols), monomer conversion (open symbols), system containing solid catalysts (squares) and system containing liquid phase only (circles). Toluene,  $40^\circ\text{C}$ , NBE/Ru molar ratio = 700,  $c_{0(\text{NBE})} = 10\text{ mg/ml}$ .

initial rate as for  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$ . However, after ca. 1 h the polymerization ceased and later stopped reaching 28% yield of the polymer only. It may suggest the surface of catalyst was blocked with the polymer, which prevented the access of monomer to the catalytic centres. These results manifest the necessity of mesoporous structure of catalysts for obtaining high yields of polymers.

In order to confirm that the catalytic activity was really bound to the solid phase the following filtration experiment was performed [ $[\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}]$ ,  $t=40^\circ\text{C}$ , molar ratio monomer/Ru = 700]. Approximately 1/3 of the liquid phase was separated by filtration after 100 min of the reaction (the polymer yield achieved at this moment was 34%) and allowed to react further under the same conditions as the rest of the reaction mixture. NBE conversions and polymer yields are presented in Fig. 5. It is evident that neither the NBE conversion nor the polymer yield increased in the liquid phase alone whereas polymerization continued in the presence of the solid catalyst reaching 72% yield of polymer at 370 min ( $M_w$  of polymer was 330 000). It proved that the catalytic activity was bound to the solid phase during polymerization.

The Ru leaching was determined in a parallel experiment carried out under the same reaction conditions as the filtration experiment. After 390 min, the polymerization was quenched, the catalyst was removed by centrifugation and the content of Ru in the liquid phase was determined. The Ru amount found was equal to 2.8% of the amount of Ru present in the catalyst and corresponds to the maximum product contamination 47 ppm.

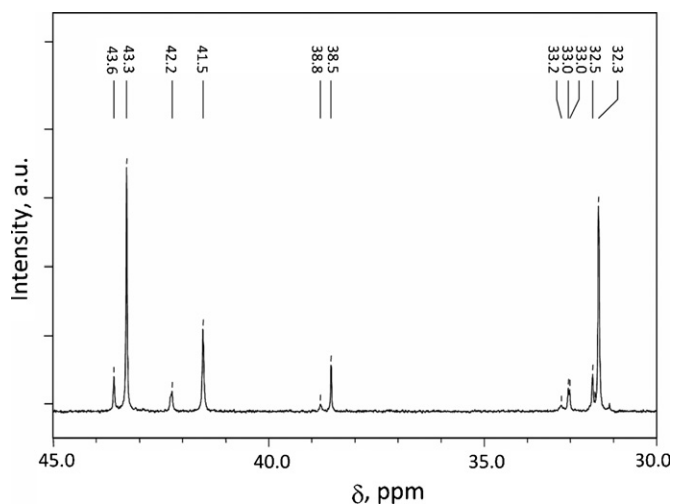
Table 1 gives the results achieved in polymerization of DCPD and NBEAc with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  used as a homogeneous catalyst and  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$ . With both catalysts and under the same reaction conditions as used for NBE, DCPD provided high molecular weight polymers (PDCPD) in high yields. Completely soluble PDCPD was obtained, which indicates no cross-linking via cyclopentene ring opening occurred. In the case of NBEAc, reaction conditions different from those applied previously had to be adopted (higher initial concentrations of monomer and catalyst, higher reaction temperature and prolonged reaction time). Under these conditions, high yields of high molecular weight polymers (PNBEAc) were achieved.

**Table 1**

Polymerization of DCPD and NBEAc with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  and with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$  catalysts.

Catalyst	Monomer	Polymer yield, %	$M_w$	$I_n$
$\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$	DCPD	86	270 000	2.3
$\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$	DCPD	79	400 000	2.1
$\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$	NBEAc	97	210 000	2.0
$\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$	NBEAc	67	330 000	2.0

Toluene, monomer/Ru molar ratio = 220 (DCPD), 50 (NBEAc),  $c_0(\text{DCPD}) = 10 \text{ mg/ml}$ ,  $c_0(\text{NBEAc}) = 50 \text{ mg/ml}$ ,  $t = 40^\circ\text{C}$  (DCPD),  $60^\circ\text{C}$  (NBEAc), reaction time 5 h (DCPD), and 20 h (NBEAc).



**Fig. 6.**  $^{13}\text{C}$  NMR spectrum (range of aliphatic C atoms) of PNBE prepared with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$ .

Both IR and NMR spectra of polymers proved the structure consistent with ROMP (Eqs. (1) and (2)). PNBEs of prevailing *trans* configuration (about 85% *trans* double bonds determined from  $^1\text{H}$  NMR signals of olefinic hydrogen at 5.22 and 5.36 ppm) were prepared in all cases in contrast to the PNBE prepared using immobilized  $[\text{RuCl}_2(p\text{-cymene})]_2$  (about 50% *trans* double bonds [33]).  $^{13}\text{C}$  NMR spectra of PNBEs provided additional information about the distribution of *cis* and *trans* double bonds throughout the polymer chains. From the intensities of  $^{13}\text{C}$  NMR signals of four possible dyads  $I_{cc}$ ,  $I_{tt}$ ,  $I_{ct}$ , and  $I_{tc}$  parameters  $r_c = I_{cc}/I_{ct}$  and  $r_t = I_{tt}/I_{tc}$  describing “blockiness” of polymer chains can be determined [18,41]. From signals of C1 and C4 atoms of PNBE prepared with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$  at  $\delta$  (ppm) 43.6 (tc), 43.3 (tt), 38.8 (cc), 38.5 (ct) (Fig. 6) following parameters were calculated:  $r_t = 4.9$  and  $r_c = 0.3$ . Practically the same parameters  $r_t = 5.2$  and  $r_c = 0.3$  were found for PNBE prepared with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  as a homogeneous catalyst. Thus, the immobilization had no effect on catalyst stereoselectivity. It suggests that catalytic centers of similar steric arrangement were operating in both homogeneous and immobilized catalysts.

#### 4. Conclusion

$\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$ , which can be easily prepared from commercially available  $[\text{RuCl}_2(p\text{-cymene})]_2$ , was immobilized on mesoporous molecular sieves MCM-41 and SBA-15 and on conventional silica. These materials were active as catalysts for ROMP of NBE, NBEAc and DCPD producing high molecular weight polymers ( $M_w$  from 200 000 to 400 000) in high yields. For NBE, the initial rate increased in the order  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{silica} \cong \text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15} < \text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$ . High yields of PNBE obtained with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{SBA-15}$  and

$\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$  (up to 80%) and relatively low yield obtained with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{silica}$  (28%) illustrate the necessity of using mesoporous catalysts for obtaining high polymer yields.

The filtration experiment proved that the catalytic activity was bound to the solid phase during the polymerization. Catalysts could be easily separated from the reaction mixture in contrast to the corresponding homogeneous system and polymers with low content of Ru were obtained.

High *trans* PNBEs were prepared with all catalysts used. No differences in the polymer microstructure (*trans* double bond content, *cis* and *trans* double bond distribution along the chains) were found for the polymer prepared with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)$  used as a homogeneous catalyst and that prepared with  $\text{RuCl}_2(p\text{-cymene})(\text{PCy}_3)/\text{MCM-41}$ . It suggests that catalytic centres of similar steric arrangements were in action in both cases.

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