

Immobilization of metal chloride complexes of titanium, zirconium, and hafnium on a cyclopentadienyl surface of silica for ethylene polymerization

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Abstract

Metal chloride complexes, $MCl_4(THF)_2$ ($M = Zr, Hf$) and $(Cp'')MCl_3$ ($M = Ti, Zr, Hf$, $Cp'' = \eta^5-C_5H_5$, or $\eta^5-C_5(CH_3)_5$), were immobilized on a cyclopentadienyl surface of silica with a help of *n*-BuLi. Before this, the silica was modified with silane coupling agent, $(EtO)_3Si(CH_2)_3Cp$, by applying saturating gas–solid reactions using atomic layer chemical vapor deposition (ALCVD) technique. The heterogeneous catalysts were characterized by FTIR, ^{13}C and ^{29}Si solid state NMR spectroscopies and elemental analyses. The prepared catalysts were tested in the polymerization of ethylene using methylaluminoxane (MAO) cocatalyst. Heterogeneous catalysts $CpZrCl_3/S$ and $CpHfCl_3/S$ ($S = (EtO)_3Si(CH_2)_3Cp$ modified silica carrier) exhibited high activities and produced polyethylene with a narrow molar mass distribution. However, the corresponding titanium catalyst, $CpTiCl_3/S$, exhibited low activity in ethylene polymerization and it dimerized and oligomerized ethylene. The activities of heterogeneous $MCl_4(THF)_2/S$ ($M = Zr, Hf$) and $[\eta^5-C_5(CH_3)_5]MCl_3/S$ ($M = Ti, Zr, Hf$) catalysts were low and they all, except $HfCl_4(THF)_2/S$ catalyst, produced polyethylene with a broad molar mass distribution. Catalyst leaching from the carrier was studied by treating the heterogeneous $CpZrCl_3/S$ catalyst with MAO. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The invention of methylaluminoxane (MAO) cocatalyst and the synthesis of *ansa*-metallocenes awakened interest of academic world and industry in metallocene catalysts in the 1980s [1]. The group IV metallocene complexes, used in polymerization, are of the form Cp'_2MX_2 and consists of two cyclopentadienyl rings ($Cp' = \eta^5-C_5H_5$, or $\eta^5-Me_5(CH_3)_5$)

attached to the metal, the two other ligands being either halogens or alkyls. Additionally, monocyclopentadienyl complexes are included into the metallocene group [2]. Metallocenes can have high activity in olefin, for example polymerization, and produce polymer with a narrow molar mass distribution. The possibility to tailor the ligand framework of metallocenes, enable the control of polymer microstructure and metallocenes can also be used to produce new type of polymer materials [3,4].

Metallocene catalysts are nowadays, in addition to conventional transition metal catalysts; the Phillips catalyst (CrO_3 on SiO_2) and the Ziegler–Natta catalyst

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(TiCl_3 or TiCl_4 on MgCl_2), used in commercial production of polyolefins [5–7]. Usually, before metallocene catalysts can be used in industry, they must be supported on carrier material [8]. The most important reasons for this are: (1) the existing technology is mainly based on heterogeneous catalysts. Heterogeneous metallocene catalysts can be used in place of conventional catalysts in existing reactors [1]. (2) With the help of heterogeneous catalysts, the morphology (particle size and shape) and bulk density of polymer particles can be controlled. This is important, because otherwise reactor fouling will cause problems [9]. The most usual way to prepare heterogeneous metallocenes is to adsorb the metallocene complex on a silica carrier that is pretreated with MAO cocatalyst. When also the cocatalyst, MAO, is heterogenized, the amount of MAO needed to activate the metallocene is smaller, which is the third benefit of heterogeneous catalyst. The homogeneous catalysts need large amounts of expensive MAO for activation [8,9]. The principles of preparation of heterogeneous catalysts are summarized, for example, by Ribeiro et al. [9] who published the first review article considering heterogeneous metallocenes. Since then new innovations have been reported in the open literature. One example, where no carrier is used, is the use of self-immobilizable metallocene complexes, which are copolymerized into the polymer chain during polymerization process [10,11]. In another method, the “in situ supported” polymerization catalyst was prepared in polymerization reactor by adding the catalyst solution directly to the surface of MAO treated SiO_2 [12,13].

In this study, heterogeneous catalysts were prepared by immobilization of metal chloride complexes on the surface of a silica carrier, which was premodified with $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ coupling agent to obtain a surface covered with cyclopentadienyl groups. In this carrier, cyclopentadienyls are linked to the surface of silica with trimethylene, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, spacer. Previously, a similarly modified silica support has been used to immobilize CpZrCl_3 on a carrier [14]. Here we report a more comprehensive study, involving various metal chlorides of Ti, Zr, and Hf. The prepared catalysts were characterized by elemental analysis, and solid state NMR and FTIR spectroscopy. To compare the activities, the heterogeneous catalysts were tested in ethylene polymerization in the presence of MAO. Possible catalyst leaching was examined to find out if

MAO is capable to desorb the chemically bound catalyst from the carrier.

2. Experimental

2.1. Reagents

All reactions were carried out under inert nitrogen atmosphere. Toluene and THF were distilled over sodium-benzophenone ketyl before use. Silica (EP10, Crosfield), preheated in air at 820°C for 16 h, had a surface area of $270\text{ m}^2/\text{g}$ and mean particle size of $100\ \mu\text{m}$. After heat treatment at 820°C silica contained $1.1\ \text{OH groups nm}^{-2}$ [15]. $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ (ABCR) was used as coupling agent. *n*-Butyllithium (2.5 M in hexane), Cp_2ZrCl_2 , CpTiCl_3 , $\text{ZrCl}_4(\text{THF})_2$, and HfCl_4 were from Aldrich and used without further purification. Cp^*TiCl_3 , Cp^*ZrCl_3 , Cp^*HfCl_3 , Cp^*HfCl_3 , Cp_2TiCl_2 and Cp_2HfCl_2 were purchased from Strem Chemicals and were used, as well as the MAO (10 and 30 wt.% in toluene, Witco), as received. $\text{HfCl}_4(\text{THF})_2$ was synthesized according to the literature [16]. Ethylene (99.95%, AGA) was purified with columns of molecular sieves and $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst.

2.2. Modification of silica

Silica was modified with $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ at 275°C in a commercial atomic layer chemical vapor deposition (ALCVD) reactor (F-120, Microchemistry) using saturating gas–solid reactions as described previously [14]. Modified carriers S1, S2, and S3 contained 5.1, 4.9, and 5.0 wt.% of carbon, respectively. On the basis of ^{29}Si NMR measurements, about one-third of the silane coupling agent was in bidentate form, so the concentration of silane in the carrier was in the range of $0.36\text{--}0.38\ \text{mmol/g}$ of carrier. These values correspond to $0.80\text{--}0.84\ \text{silane molecules nm}^{-2}$ of carrier.

2.3. BuLi treatment of modified silica

In a typical procedure, excess of *n*-BuLi (ca. 2 ml of 2.5 M solution in hexane) in proportion to the amount of silane on the carrier was dissolved in THF (20 ml) and added in small portions to the mixture of modified carrier (ca. 3 g) and THF (50 ml). The mixture was left

overnight under stirring and finally it was filtrated and washed with THF (3×20 ml). Solvent was removed from the carrier under vacuum.

2.4. Immobilization of metal chlorides on the carrier

Excess of metal chloride complex (e.g. 360 mg of CpHfCl_3) was dissolved in THF (40 ml) and added in small portions to the suspension of BuLi treated carrier (1.97 g of S1) and THF (30 ml). The reaction mixture was left overnight under stirring at room temperature. Finally, the obtained catalyst was filtrated, washed with THF (3×30 ml) and the solvent was removed under vacuum. All the supported catalysts were synthesized using similar procedure as above, but heterogeneous $\text{Cp}^*\text{ZrCl}_3/\text{S3}$ and $\text{CpTiCl}_3/\text{S2}$ catalysts were protected from light during the synthesis and storage. The amounts of reagents in the synthesis of catalysts are reported in Table 1.

2.5. Characterization of the supported catalysts

Elemental analyses were conducted with a Carlo Erba Instruments EA 1110 elemental analyzer. Metal contents of the catalysts were determined with inductively coupled plasma atomic emission spectrometer (ICP).

2.5.1. FTIR

The heterogeneous catalysts and homogeneous metal complexes were characterized under nitrogen with the Nicolet Impact 400 D FTIR spectrometer using diffuse reflectance technique (DRIFT). Homogeneous catalyst samples were dispersed in KBr and measured as a powder.

2.5.2. NMR

CP (cross-polarization) MAS (magic-angle spinning) NMR measurements of modified carriers and heterogeneous catalysts were carried out with a Bruker AMX-400 FT NMR spectrometer. The samples were packed in 7 mm ZrO_2 rotors equipped with KEL-F caps and the spinning rate was 4500 Hz. Solution (THF) was removed from NMR samples before measurements by keeping the samples at vacuum for prolonged times. ^{13}C NMR (100.61 MHz): contact time of 3 ms, delay of 4 s, and reference glycine (C=O carbon at 176.1 ppm). ^{29}Si NMR

(79.49 MHz): contact time of 5 ms, delay of 5 s, reference octa(trimethylsilyl)octasiloxane ($\text{Si}(\text{CH}_3)_3$ silicons at 11.47 and 11.67 ppm).

2.6. Polymerization experiments

Polymerizations were carried out in 0.5 dm³ thermostated stainless steel reactor. Toluene, MAO and the suspension of catalyst in toluene were added to the reactor. The total volume of polymerization medium was 300 ml. The mixture was stirred and polymerization reaction was initiated by introducing ethylene into the reactor. Polymerization temperature and partial pressure of ethylene were kept constant during reaction. Polymerization was stopped by adding dilute HCl solution in ethanol. The product was isolated by filtering and washed with ethanol.

The total consumption of ethylene (consists of filling of the reactor and consumption during the polymerization reaction) was followed in each experiment through a mass flow meter and reported in milliliters (at NTP). Using the ideal gas law, an ethylene consumption of 1000 ml corresponds to about 1.25 g of polyethylene. The amount of ethylene needed to fill the reactor to ethylene over pressure of 2 bars at 60 °C was deduced with the help of background experiment. This experiment was conducted like normal polymerizations, but without the catalyst and 15 ml of 10 wt.% MAO was added to the reactor. No polymer was found in the reactor and total consumption of ethylene was 1500 ml.

2.7. Polymer characterization

Melting temperatures (T_m) were determined with a Mettler Toledo DSC821 differential scanning calorimeter. The melting endotherms were measured for samples which had been previously heated to 180 °C and cooled down. Polymer samples were heated at a rate of 10 °C/min. Molar masses and molar mass distributions were measured with Waters 150-C gel permeation chromatograph operating at 140 °C and equipped with four Waters Styragel columns (HMW2, 2 \times HMW6E, HMW7) and an RI detector. Solvent, 1,2,4-trichlorobenzene was applied at a flow rate of 1.0 cm³/min. The columns were calibrated with a narrow molar mass distribution polystyrene standards using a universal calibration method.

Table 1
Synthesis of heterogeneous catalysts and their metal and chlorine contents

Catalyst no.	Immobilized metal chloride/carrier ^a	Concentration of silane on carrier (mmol/g) ^b	Amount of BuLi-modified carrier (g)	Amount of metal complex (mg)	Metal content of heterogeneous catalyst (wt.%)	Cl content of heterogeneous catalyst (wt.%)	Metal/silane ratio (mol/mol)	Cl/M ratio (mol/mol)
1	ZrCl ₄ (THF) ₂ /S1	0.38	2.1	353	5.0	3.4	1.5	1.7
2	HfCl ₄ (THF) ₂ /S2	0.36	1.0	156	6.6	1.7	1.0	1.3
3	CpTiCl ₃ /S2	0.36	2.0	312	2.2	– ^c	1.3	–
4	CpZrCl ₃ /S3	0.37	3.0	350	3.3	0.7	1.0	0.6
5	CpHfCl ₃ /S1	0.38	2.0	360	6.0	1.3	0.9	1.1
6	Cp*TiCl ₃ /S3	0.37	1.9	231	1.3	0.3	0.7	0.3
7	Cp*ZrCl ₃ /S3	0.37	1.0	148	2.1	0.5	0.6	0.6
8	CP*HfCl ₃ /S1	0.38	1.8	418	3.1	0.7	0.5	1.1

^a S1, S2, and S3 are three lots of (EtO)₃Si(CH₂)₃Cp-modified silica carriers.

^b Estimated value, which is based on carbon content of the (EtO)₃Si(CH₂)₃Cp-modified silica carrier and that one third of the silane on carrier is in bidentate form.

^c Not analyzed.

2.8. Gas chromatographic analyses

The oligomeric products of the polymerizations were analyzed with HP 6890 gas chromatograph equipped with a HP 7683 injector, a 60 m capillary column (HP-1) and FI detector. Helium was used as a carrier gas.

2.9. Catalyst treatment with MAO

A mixture of heterogeneous CpZrCl₃/S3 (**4**) catalyst (110 mg, 40 μmol of Zr), 10 wt.% MAO (26 ml), and toluene (10 ml) were stirred at room temperature for 1 h. The solution part of the mixture was separated by filtering and the remaining solid was washed with toluene. In this experiment, the mole ratio of aluminum to zirconium was 1000. The activity of the formed solution was tested by adding the filtrate to the polymerization reactor. For comparison, one polymerization was conducted with the untreated heterogeneous CpZrCl₃/S3 (**4**) catalyst (110 mg, 40 μmol of Zr) under the same reaction conditions and using an Al/Zr mole ratio of 1000, see Table 5 for results.

3. Results and discussion

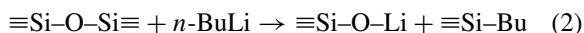
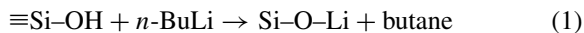
3.1. Modification of silica

Modified silica carriers S1, S2, and S3 were prepared by a reaction of silica, preheated at 820 °C, with vaporized silane coupling agent, Cp(CH₂)₃Si(OEt)₃, at 275 °C in ALCVD reactor until the surface was saturated. In gas phase modification, only one molecular layer is formed and the silane coupling agent is attached to the surface with one (monodentate silane) or two (bidentate silane) chemical bonds (Scheme 1). Modification is continued until the triethoxysilane compound has reacted with all the available adsorption sites, for example, –SiOH groups, on the surface. The coupling agent can react with the siloxane bridges [17], too, especially, when the silica has been preheated at relatively high temperature [18]. This has been observed previously when silicas, preheated at 600 and 820 °C, were modified with aminopropyl-dimethylethoxysilane [(EtO)(Me)₂Si(CH₂)₃NH₂] [18]. In the reaction of Cp(CH₂)₃Si(OEt)₃ with

≡Si–O–Si≡ bridges, surface ≡Si–OEt groups are formed, as well.

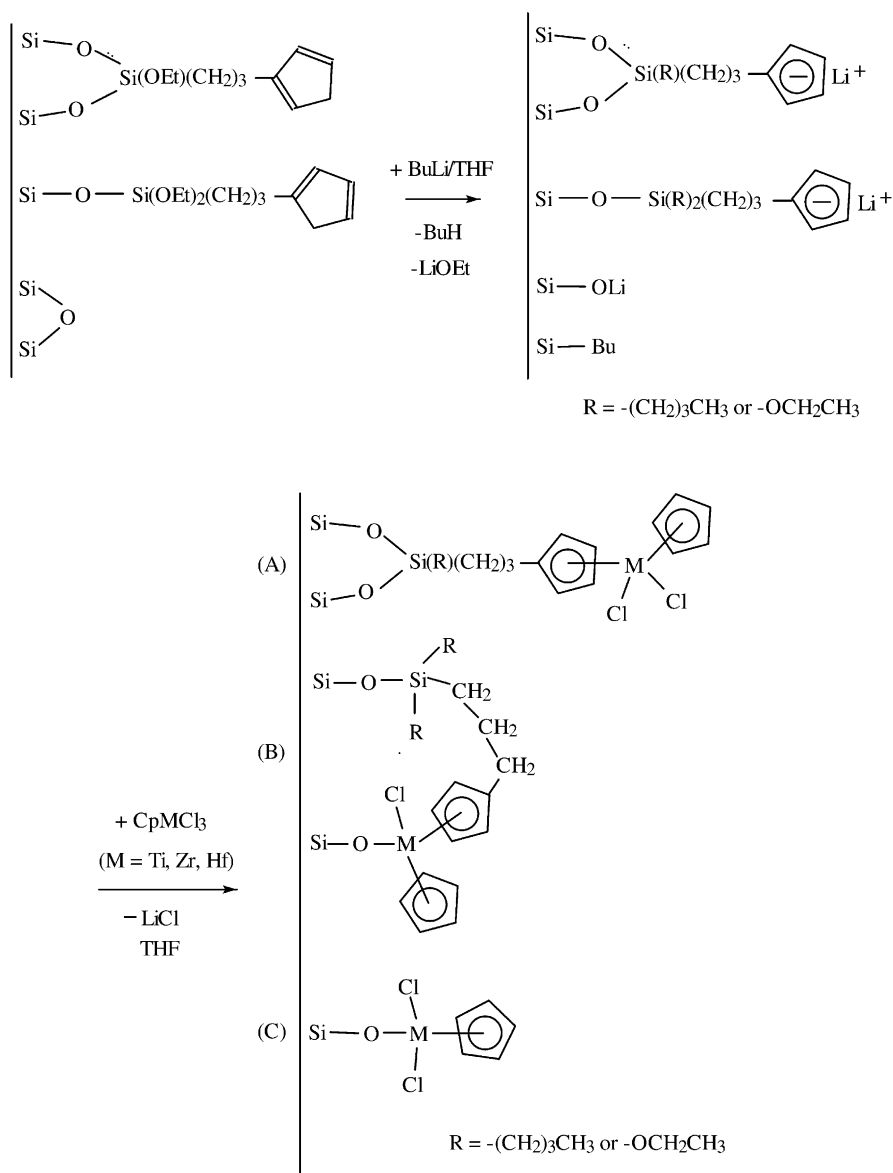
3.2. Catalyst synthesis

In this paper, we report the synthesis of eight heterogeneous catalysts, where the metal (Ti, Zr, or Hf) and the ligands (Cp, Cp* = C₅(CH₃)₅, and Cl) were varied. The syntheses of heterogeneous catalysts are reported in Table 1. Scheme 1 illustrates catalyst synthesis and possible structures that may be formed when CpMCl₃ (or Cp*MCl₃) (M = Ti, Zr, Hf) complexes are adsorbed onto the modified silica carrier. Modified carriers were treated with *n*-butyllithium before chemisorption of metal complexes onto the carrier. *n*-BuLi was used in excess in proportion to the estimated amount of silane on the carrier. Also metal chlorides were added in excess in relation to silane. Based on the metal analysis, 30–80% of used metal was adsorbed on the carrier. Exceptions were the synthesis of heterogeneous MCl₄(THF)₂ (M = Zr (**1**) or Hf (**2**)) catalysts, where lower amounts of metal complex were used and where all the metal complex seemed to adsorb on the carrier. Possible catalyst structures (A–G) that may be formed on the carrier are shown in Schemes 1 and 2. Species B, C, F, and G are possible if the metal complexes react with ≡Si–O–Li groups on the carrier. These latter moieties are formed when *n*-butyllithium reacts with the ≡Si–OH groups of silica but also in the reaction with siloxane ≡Si–O–Si≡ bridges [19] (Eqs. (1) and (2)).



Reaction of *n*-BuLi with ≡Si–O–Si≡ linkages of silica have been suggested [19,20]. Moreover, the ²⁹Si CP MAS NMR [21,22] studies of MeLi treated silica have confirmed the capability of alkyllithium reagents to react with ≡Si–O–Si≡ groups. Different types of metal sites may form on the carrier, because metal complex can bound to the surface, besides with Cp'–M linkages, also with Si–O–M bonds. As a consequence the molar mass distributions would become broad in the polymerization experiments.

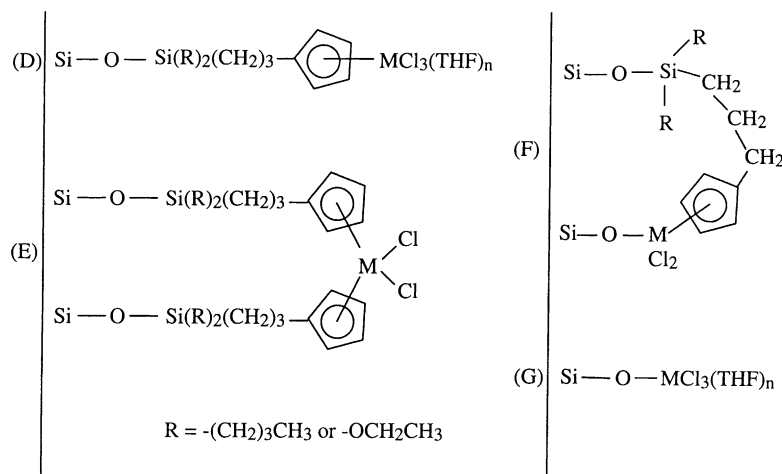
The metal contents of the heterogeneous catalysts were relatively high, for example, the Hf contents



Scheme 1. Immobilization of CpMCl_3 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) complexes on a cyclopentadienyl surface of silica with a help of *n*-BuLi.

were 6.6, 6.0, and 3.1 wt.% of Hf for the three heterogeneous $\text{HfCl}_4(\text{THF})_2/\text{S2}$ (**2**), $\text{CpHfCl}_3/\text{S1}$ (**5**), and $\text{Cp}^*\text{HfCl}_3/\text{S1}$ (**8**) catalysts, respectively. When the size of the ligands in a metal complex increases, less metal is adsorbed on the carrier. Similar trends were observed for titanium and zirconium catalysts, too. Moreover, the size of the metal affected the metal contents

(at a coordination number of 8 and oxidation number of IV the ionic radii are 0.88, 0.98, and 0.97 Å for Ti, Zr, and Hf, respectively [23]). More titanium was bound to the surface when compared to the metal contents in the corresponding Zr and Hf catalysts. This can be seen by comparing the mole ratio of metal to silane of following heterogeneous catalysts: $\text{CpTiCl}_3/\text{S2}$ (**3**)



Scheme 2. Possible surface structures that may be formed when $\text{MCl}_4(\text{THF})_2$ ($\text{M} = \text{Zr}, \text{Hf}$) complexes are immobilized on $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ -modified silica carrier.

(Ti/silane = 1.3), $\text{CpZrCl}_3/\text{S3}$ (**4**) (Zr/silane = 1.0), and $\text{CpHfCl}_3/\text{S1}$ (**5**) (Hf/silane = 0.9).

When the metal to silane mole ratios of heterogeneous catalysts in Table 1 are near a value of 1 or below it, approximately each metal complex is bound to only one surface cyclopentadienyl (Cp') group. Consequently, when CpZrCl_3 or CpHfCl_3 complexes are immobilized on carrier bis(cyclopentadienyl) species are formed on the surface. In the case of heterogeneous $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{MCl}_3$ catalysts **6–8**, the metal/silane mole ratio is lower (between 0.5 and 0.7), presumably because the bigger size of the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand has hindered adsorption of $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{MCl}_3$ complexes to all surface Cp' groups.

In the case of heterogeneous $\text{ZrCl}_4(\text{THF})_2/\text{S1}$ (**1**) and $\text{CpTiCl}_3/\text{S2}$ (**3**) catalysts, metal to silane ratios are 1.5 and 1.3, respectively. Formation of species (silica)–Si–O– ZrCl_3 (structure G in Scheme 2) and (silica)–Si–O– TiCl_2Cp (structure C in Scheme 1) would explain the higher metal contents. Thus, there seems to be two types of metal species on the carrier in catalysts **1** and **3**, which can lead to a broad molar mass distribution in ethylene polymerization tests.

The chlorine contents of the heterogeneous catalysts are reported in Table 1. The chlorine contents are low and indicate that the metal complexes have reacted with the surface through their chlorine atoms. For

example, for heterogeneous $\text{CpHfCl}_3/\text{S1}$ (**5**) catalyst the Cl/Hf mole ratio is only 1.1. This means that CpHfCl_3 complex would be attached to the surface with two linkages; one bond is formed between surface Cp' group and hafnium and the other bond is possibly Hf–O–Si bond. Thus, the structure of heterogeneous $\text{CpHfCl}_3/\text{S1}$ (**5**) catalyst would be of the form $\text{Cp}'\text{CpHfCl}(\text{O}-\text{Si}\equiv)$ (structure B in Scheme 1). The mole ratios of chlorine to metal, suggests similar M–O–Si \equiv linkages for other catalysts, as well. Spectral characterization (FTIR, ^{29}Si NMR, see Section 3.3) of carriers and the polymerization experiments (Section 3.4) did not fully support this conclusion, and an additional analysis method of chlorine would be necessary to confirm the metal/chlorine mole ratios.

Because, the active form of group IV metallocene catalyst is believed to be methylated cationic complex, $[\text{Cp}_2\text{M}(\text{CH}_3)]^+$ [24], the surface species which are attached to the surface through M–O–Si \equiv bonds as in structure B are not expected to be active in the polymerization, unless MAO is capable to dissociate the M–O bond so that cationic Ti, Zr, or Hf species are formed. There are studies where breakage of M–O–Si bond ($\text{M} = \text{Ti}, \text{Zr}$) has been suggested by MAO, for example, in the case of silsesquioxane complexes of Ti and Zr [25,26] and silica supported zirconium complexes [27] (this is further discussed in the context of polymerization results in Section 3.4).

Table 2

Selected IR bands (in cm^{-1}) of Cp groups of modified silica carriers and heterogeneous and homogeneous catalysts^a

Sample	$\nu(\text{C-H})_{\text{Cp}'}$ (carrier)	$\nu(\text{C-H})_{\text{Cp}}$ (complex)	$\pi(\text{C-H})_{\text{Cp}}$ area: 800–900 cm^{-1}	Combination bands in area 3920–3950 cm^{-1}
Carriers	3044–3047 (br), 3092–3095 (w)			
BuLi/carrier	3036–3044 (sh)			
ZrCl ₄ (THF) ₂ /S1	3042 (br)			
HfCl ₄ (THF) ₂ /S2	3042 (br)			
CpTiCl ₃ /S2	3041 (br)	3109 (br)		3944 (br)
CpZrCl ₃ /S3	3038 (sh)	3090 (sh), 3107 (br)		3944 (br)
CpHfCl ₃ /S1	3045 (sh)	3092 (sh), 3117 (br)		3947 (br)
Cp*TiCl ₃ /S3	3038 (sh)			
Cp*ZrCl ₃ /S3	3040 (sh)			
CP*HfCl ₃ /S1	3040 (sh)			
Cp ₂ TiCl ₂		3103 (s)	821 (s), 873 (m)	3923 (m), 3943 (sh)
Cp ₂ ZrCl ₂		3100 (s)	811 (s), 840 (s, br)	3926 (sh), 3939 (m)
CpHfCl ₃		3110 (s)	832 (s)	3941 (m, br)
Cp ₂ HfCl ₂		3103 (s)	818 (s), 842 (sh, br)	3942 (m)
CP*HfCl ₃				3935 (w, br)

^a Homogeneous complexes were dispersed in KBr before measurement. Symbols— ν : stretching, π : out-of-plane bending. Signal intensity—s: strong; m: medium; w: weak; br: broad.

In the case of heterogeneous ZrCl₄(THF)₂/S3 (**1**) and HfCl₄(THF)₂/S1 (**2**) catalysts, the monocyclopentadienyl surface species of the form ($\equiv\text{Si-O}$)Cp'MCl₂ (Cp' = surface Cp group, M = Zr, Hf) (species F in Scheme 2) can be active in polymerization, because homogeneous monocyclopentadienyl complexes having alkoxo ligands have been found active in alkene polymerizations in the presence of MAO. Examples are $[\eta^5\text{-C}_5(\text{CH}_3)_5\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)\text{Cl}_2]$ [28] and different Cp'TiCl₂(O-Ar) (Cp' = C₅H₅, C₅(CH₃)₅, Ar = aryl group) complexes [29,30].

3.3. Characterization of catalysts

The IR and NMR spectra of heterogeneous hafnium catalysts are discussed in detail, similar features are found in the corresponding spectra of Ti and Zr catalysts, too. Important IR bands and ¹³C NMR resonances of the carriers and the catalysts are listed in Table 2 (IR) and Table 3 (NMR).

3.3.1. FTIR spectra

FTIR spectra of modified carrier (S1) and the same carrier after *n*-BuLi treatment are shown in Fig. 1. The absence of a Si–OH band at 3745 cm^{-1} denotes that all the isolated $\equiv\text{Si-OH}$ groups of silica

have reacted with the silane coupling agent (Fig. 1a), but there are some hydrogen bonded silanol groups (band at 3430–3460 cm^{-1}) left in the carrier. These are either inside the silica structure or on the surface

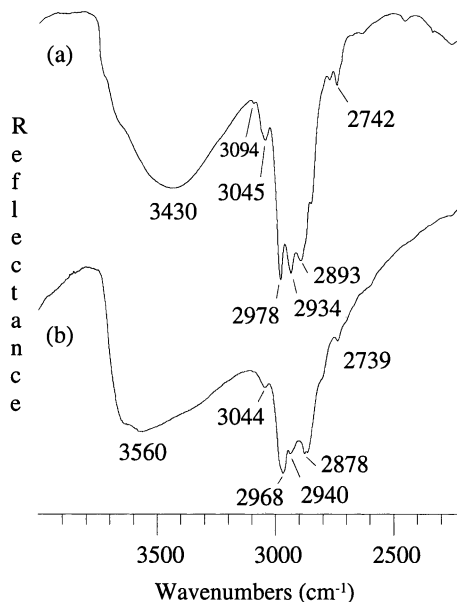


Fig. 1. FTIR spectra of (a) (EtO)₃Si(CH₂)₃Cp-modified silica carrier (S1) and (b) same carrier after *n*-BuLi treatment (BuLi/S1).

Table 3
 ^{13}C NMR chemical shifts of carriers and heterogeneous catalysts (values in ppm)^a

Sample	Spacer: CH ₂ , Bu: CH ₃ , Cp*: CH ₃	EtO: CH ₃ , Bu: CH ₂	Spacer: CH ₂ , Bu: CH ₂ , THF: CH ₂	Spacer: CH ₂ , Bu: CH ₂	Cp'	EtO: CH ₂	Cp or Cp*	M-THF	Solvent: THF: CH ₂
Cp-modified carriers (S1–S5)	10–11 (m)	16 (s)	20–21 (m)	32–33 (m)	42 (w), 127 (w), 145 (w)	58 (s)			
<i>n</i> -BuLi treated carriers	12 (w)	17–19 (m or s)	25–26 (s)	32 (w or m), 34–35 (w or m)	42–45 (w), 125–129 (w), 144–147 (w)	58 (m or s)			68–69 (m)
ZrCl ₄ (THF) ₂ /S1	11 (m)	16 (s), 17 (sh)	21 (m), 24 (m)	34 (m), 32 (sh)	42, 127, 145	58 (s)		72 (w)	68 (w)
HfCl ₄ (THF) ₂ /S2	11 (m), 12 (m)	16 (s), 18 (sh)	21 (sh), 25 (s)	32 (m)	45, 125, 145	58 (s)		72 (m)	69 (m)
CpTiCl ₃ /S2	12 (m)	16 (m), 17 (sh)	22, 25 (m), 29 ^d (m)	32 (m), 34 (sh)	42, 125, 145	58 (s)	117 (s)		68 (w)
CpZrCl ₃ /S3	12 (m)	16 (s)	21 (sh), 23 (sh), 25 (s)	33 (m)	43, 128, 147	58 (s)	114 (s)		69 (s)
CpHfCl ₃ /S1	12 (s)	16 (sh), 18 (m)	22 (sh), 25 (sh), 26 (s)	32 (sh), 34 (m)	very weak signals	58 (m)	113 (m)		68 (m)
Cp*TiCl ₃ /S3	10 (s)	16 (m)	21 (m), 25 (m)	32 (m)	45, 143	58 (m)	126 (m)		68 (w)
Cp*ZrCl ₃ /S3	10 (s)	16 (s), 17 (sh)	25 (s)	32 (m)	43, 125, 145	58 (s)	121 (m)		69 (m)
Cp*HfCl ₃ /S1	10 (sh), 12 (s)	16 (m), 18 (sh)	22 (sh), 25 (sh), 26 (s)	32 (sh), 34 (m)	very weak signals	58 (m)	117 (m)		69 (m)

^a Signal intensity—s: strong; m: medium; w: weak; sh: shoulder.

but incapable, for instance, for steric reasons, to react with the silane. The estimated amount of silane, 0.80–0.84 molecules nm^{-2} of carriers, is close to the total hydroxyl content of the starting silica material (1.1 OH nm^{-2} in SiO_2 heated at 820 °C [15]).

After *n*-BuLi treatment, changes in the bands of cyclopentadienyl groups of modified silica at 3044–3047 and 3092–3095 cm^{-1} were noticed. The latter band disappeared and the size of the former was diminished indicating that *n*-BuLi had reacted with the surface Cp' groups. When comparing the hydroxyl areas of the FTIR spectra of carriers before and after *n*-BuLi treatment, the amount of Si–OH groups did not seem to change. Thus, BuLi did not seem to react with the residual $\equiv\text{Si-OH}$ groups of carrier.

After immobilization of metal chlorides on the surface, new bands could be detected in the IR spectrum of heterogeneous ($\eta^5\text{-C}_5\text{H}_5$)HfCl₃/S1 (**5**) catalyst (Fig. 2b). New band, typical for pentahapto ($\eta^5\text{-Cp}$) complexes, at 3117 cm^{-1} is due to C–H stretching of Cp ring. The band at 3947 cm^{-1} can be assigned to a combination band of C–H stretching and C–H out-of-plane bending of Cp group [31,32]. The origin of the band at 3947 cm^{-1} can be seen in the IR spectra of homogeneous complexes, Cp₂HfCl₂ or CpHfCl₃ (see Fig. 3 and Table 2), where the signals of carrier do not overlap with the bands of Cp groups of metallocene complexes. For example, in the spectrum of Cp₂HfCl₂, there is one C–H stretching vibration of Cp at 3103 cm^{-1} and there are two out-of-plane C–H bendings at 818 and 842 cm^{-1} . The sum of the bands at 3103 and 842 cm^{-1} is 3945 cm^{-1} and this value is near the observed combination band at 3942 cm^{-1} (Fig. 3).

3.3.2. NMR spectra

3.3.2.1. ¹³C NMR spectra. The ¹³C CP MAS NMR spectra of modified carrier (S1) and carrier after *n*-BuLi treatment, including the interpretation, are shown in Fig. 4. The strongest resonances, at 16 and 58 ppm, in the spectrum of carrier in Fig. 4a, belong to unreacted ethoxy groups of silane coupling agent and to surface $\equiv\text{Si-OEt}$ groups, which are formed when the silane coupling agent reacts with siloxane bridges, $\equiv\text{Si-O-Si}\equiv$, of silica. In the synthesis, the proportion of BuLi to estimated silane concentration on the carrier varied. The best alkylation result, that

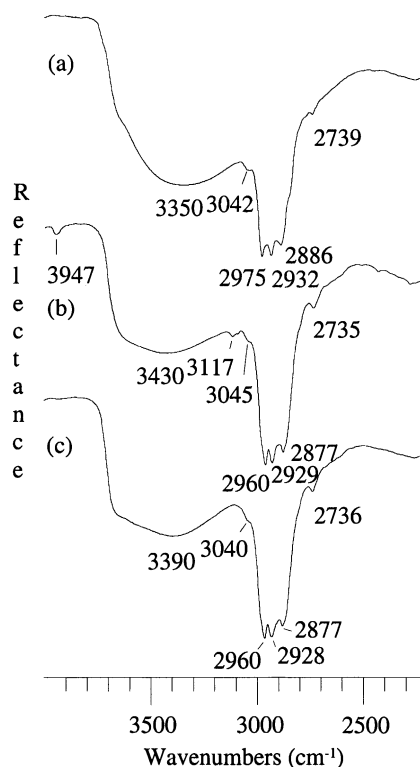


Fig. 2. FTIR spectra of carriers after modification with *n*-BuLi and immobilization of metal complexes on the carriers: (a) HfCl₄(THF)₂ on carrier S2 (**2**); (b) CpHfCl₃ on carrier S1 (**5**), and (c) Cp*HfCl₃ on carrier S1 (**8**).

is, less $\equiv\text{Si-OEt}$ groups left in the carrier, was obtained when carrier S1 was treated with a big excess of *n*-BuLi (Fig. 4b). In *n*-BuLi treated carrier in the area 10–35 ppm, the carbon resonances due to the CH₂ and CH₃ carbons of Bu groups, (–CH₂)₃ spacer, solvent (THF) and EtO-groups overlap. Butyl groups give resonances at 12, 17–19, 26, and 34–35 ppm. Additionally, in the ¹³C NMR spectrum of BuLi/carrier the signals of Cp groups are broader than in the spectrum of the original carrier due to reaction with *n*-butyllithium.

The ¹³C CP MAS NMR spectra of carriers S2 and S3 after BuLi treatment (BuLi/S2 as a support for catalyst **1** in Fig. 5a) showed, that they contained more EtO-groups than carrier S1 in Fig. 5b. In regard to catalyst activity, it would be beneficial to remove the remaining ethoxy groups from the carrier because Lewis

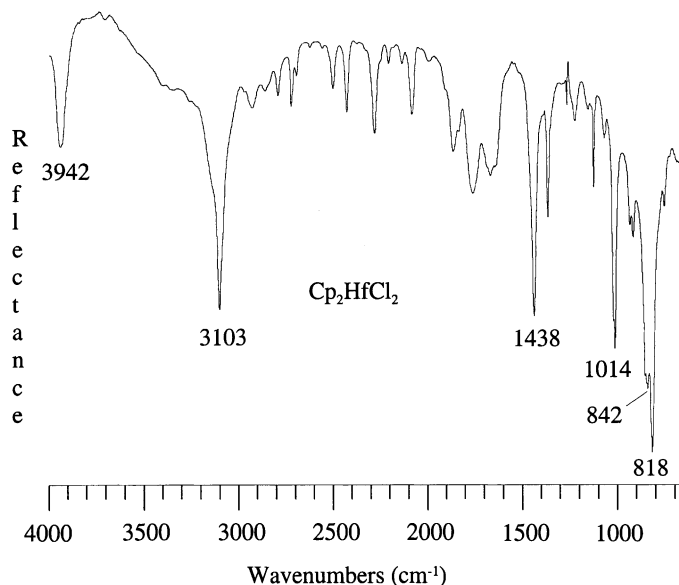


Fig. 3. FTIR spectrum of Cp_2HfCl_2 complex (in KBr).

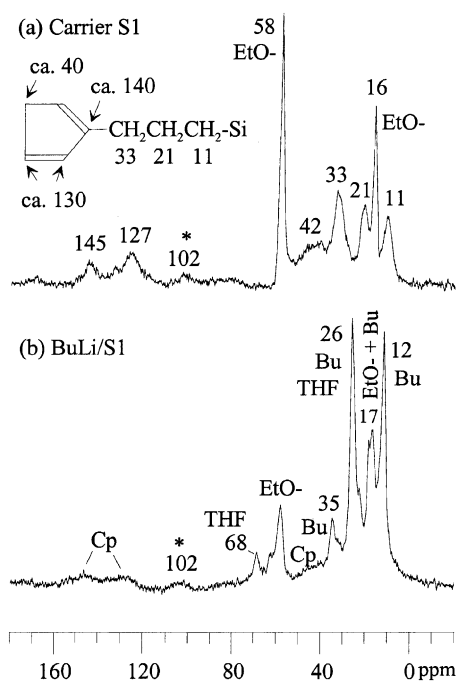


Fig. 4. ^{13}C CP MAS NMR spectra of (a) $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ -modified silica carrier (S1); (b) same carrier after $n\text{-BuLi}$ treatment. Asterisks (*) denote spinning side bands.

bases (e.g. EtO-groups and residual THF) may interfere the polymerization process.

After reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{HfCl}_3$ and $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{HfCl}_3$ with the carrier (S1), signals of aromatic carbons appeared at 113 and 117 ppm, respectively, with spinning side bands (Fig. 5b and c). The methyl groups of $[\eta^5\text{-C}_5(\text{CH}_3)_5]^-$ moiety gave a signal at 10 ppm. The ^{13}C NMR spectrum of $\text{HfCl}_4(\text{THF})_2/\text{S2}$ (**2**) catalyst (in Fig. 5a) does not differ much from the spectrum of the BuLi treated support. The only new signal in comparison with the latter is at 72 ppm and can be assigned to THF that is coordinated to hafnium. Bis(tetrahydrofuran) adducts are known for CpZrCl_3 [33] and CpHfCl_3 [34].

3.3.2.2. ^{29}Si NMR spectra. ^{29}Si CP MAS NMR spectra of modified carrier before and after $n\text{-BuLi}$ treatment as well as the interpretation of the signals are presented in Fig. 6. In the spectrum of carrier S1, the signal at -52 ppm belongs to monodentate form of the silane coupling agent, and the shoulder at -58 ppm to bidentate form. Judging from the ^{29}Si NMR with a help of spectral deconvolution, about one third of the silane was in bidentate form. Next to the broad signal of siloxane groups at -109 ppm,

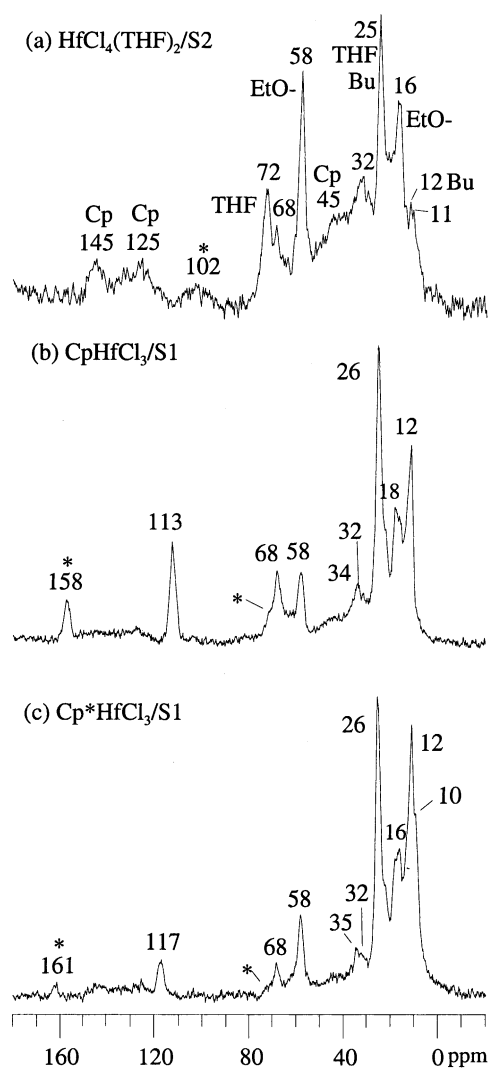
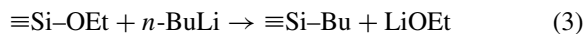


Fig. 5. ^{13}C CP MAS NMR spectra of heterogeneous catalysts; (a) $\text{HfCl}_4(\text{THF})_2$ on carrier S2 (2); (b) CpHfCl_3 on carrier S1 (5), and (c) Cp^*HfCl_3 on carrier S1 (8). Asterisks (*) denote spinning side bands.

the remaining $\equiv\text{Si}-\text{OH}$ groups should give a signal at -100 ppm according to the literature [35]. Because this signal was not resolved in the spectra of carriers S1, S2, and S3, the amount of $\equiv\text{Si}-\text{OH}$ was relatively small.

In the reaction of the modified support with *n*-butyllithium, part of the unreacted ethoxy groups of silane coupling agent and ethoxy groups on the surface of SiO_2 are alkylated (Eq. (3)) and new signals

appear at -17 , 3 , and 14 ppm, due to silicons having butyl groups (Fig. 6b).



The amount of possible surface $(-\text{O})_3\text{Si}-\text{Bu}$ groups was either small or their resonance was overlapped because they could not be assigned with certainty.

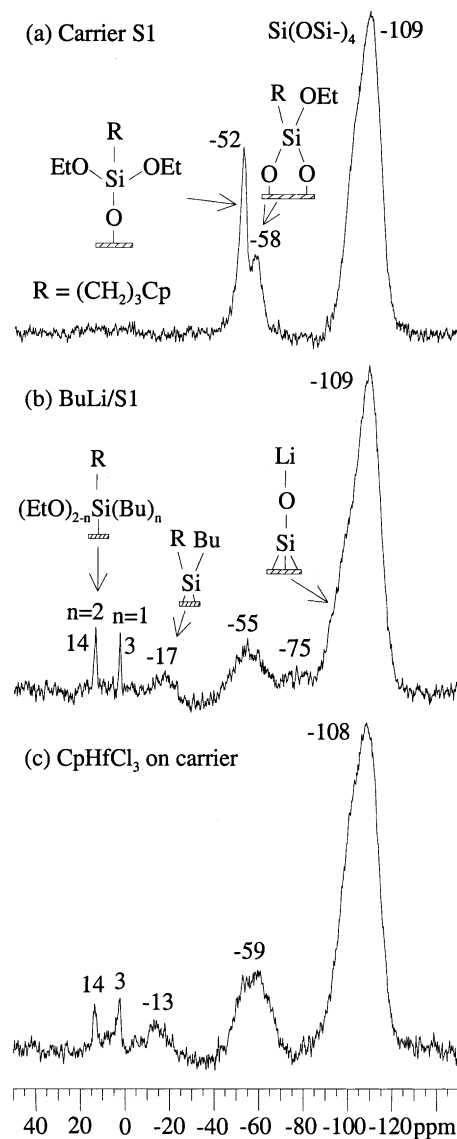


Fig. 6. ^{29}Si CP MAS NMR spectra of (a) $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ -modified silica carrier (S1), (b) same carrier after *n*-BuLi treatment, and (c) CpHfCl_3 on BuLi/S1 carrier (5) $\text{R} = (\text{CH}_2)_3\text{Cp}$.

This suggests that the amount of $\equiv\text{Si}-\text{OLi}$ groups, formed according to the Eq. (2), was small. In the spectrum of the BuLi treated carriers, there was one weak resonance at -70 – (-75) ppm which could belong to $(-\text{O})_3\text{Si}-\text{Bu}$ groups, because $(\text{O})_3\text{Si}-\text{R}$ (R = alkyl) silicons have been reported to give a signal at -60 to -73 ppm [22,35,36]. However, the signal at -70 to -75 ppm disappeared after immobilization of metal chlorides on carrier. The broad signal at -17 ppm could be due to $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{Bu})(\text{O}-)_2$ groups and possibly surface $(-\text{O})_2\text{Si}(\text{Bu})_2$ groups, because $(-\text{O})_2\text{Si}(\text{Me})_2$ groups have been reported at -15 to -20 ppm [21,22].

After *n*-BuLi treatment, the signal due to siloxane bridges, $\equiv\text{Si}-\text{O}-\text{Si}\equiv$, at -109 ppm was broader (Fig. 6b) than in the spectrum of carrier (Fig. 6a) indicating changes at silicon having four oxygen atoms around them ($\text{Si}(\text{O}-)_4$). The broadening could be due to $(-\text{O})_3\text{Si}-\text{OLi}$ groups, which resonate at -95 ppm [21].

When CpHfCl_3 was immobilized on the surface, changes in the ^{29}Si NMR spectrum when compared

to that of carrier are small. The intensity of the signal in the area -45 to -70 ppm has increased, but can be explained with a help of the used cross-polarization technique, where the intensity of the signals depends on the amount and distance of hydrogens nearby the silicons [36].

3.4. Polymerization experiments

Ethylene polymerization results with homogeneous and heterogeneous catalysts are listed in Table 4. The polymerization conditions were unoptimized and MAO was used as cocatalyst in all these experiments. The activities of heterogeneous $\text{CpZrCl}_3/\text{S3}$ (**4**) and $\text{CpHfCl}_3/\text{S1}$ (**5**) catalysts were high ($A = 400$ kg of PE/(mol Mh) in experiments 4a and 5a), but lower than the activities of corresponding homogeneous catalysts Cp_2ZrCl_2 (**10**) ($A = 14\,250$ kg of PE/(mol Zr h)) and Cp_2HfCl_2 (**11**) ($A = 1500$ kg of PE/(mol Hf h)). Generally, zirconium catalysts are more active than corresponding hafnium catalysts [4]. Now the activity of heterogeneous $\text{CpZrCl}_3/\text{S3}$ (**4**) catalyst was

Table 4
Ethylene polymerization results with heterogeneous and homogeneous catalysts^a

Catalyst number and name ^b	Experiment	Amount of catalyst (μmol)	Al/M	T ($^\circ\text{C}$)	Time (min)	Yield (g)	Activities ^c	T_m ($^\circ\text{C}$)	M_w (g/mol)	M_w/M_n
1 $\text{ZrCl}_4(\text{THF})_2/\text{S1}$	a	56.5	900	60	20	0.39	10	136.8	679000	5.3
2 $\text{HfCl}_4(\text{THF})_2/\text{S2}$	a	20.3	2000	60	60	0.52	25	125.5	309000	2.6
3 $\text{CpTiCl}_3/\text{S2}$	a	46.1	1600	40	20	0.23	14	124.5	3900, 469000 ^d	Very broad
4 $\text{CpZrCl}_3/\text{S3}$	b	45.9	2000	60	20	0.15	9	123.3		
	a	22.8	2000	60	20	3.00	400	137.2	343000	2.3
5 $\text{CpHfCl}_3/\text{S1}$	b	24.4	2000	80	12	4.20	870	136.1	111000	2.0
	a	19.4	2100	60	20	2.60	400	136.8	504000	2.3
6 $\text{Cp}^*\text{TiCl}_3/\text{S3}$	b	20.3	300	60	20	2.50	210	139.1		
	a	25.8	2100	50	20	0.55	21	123 (sh), 133.2	3900, 360000 ^d	Very broad
7 $\text{Cp}^*\text{ZrCl}_3/\text{S3}$	a	16.8	2000	80	60	0.39	21	136.9	198000	8.8
8 $\text{Cp}^*\text{HfCl}_3/\text{S1}$	a	11.4	1900	80	60	0.53	46	135.3	187000	10.9
9 Cp_2TiCl_2	a	1.2	2000	60	20	0.78	1880	139.5	383000	2.6
	b	1.1	2000	50	20	0.97	2600	139.1		
10 Cp_2ZrCl_2	a	1.2	2000	60	20	5.50	14250	136.3	254000	2.8
11 Cp_2HfCl_2	a	1.3	2000	60	20	0.69	1500	138.4	275000	2.8

^a Polymerization conditions: 300 ml of toluene as polymerization medium, ethylene over pressure of 2 bar, except in experiment 8a: 3 bars, stirring speed: 400 rpm. Cocatalyst 30 wt.% MAO; but 10 wt.% MAO in runs 9–11.

^b S1, S2, and S3 are three lots of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ -modified silica carriers.

^c Activities in kg of PE/(mol of metal h).

^d In the GPC experiments, two, partly overlapping, molecular weight distributions were observed, which were calculated separately.

near the activity of corresponding hafnium catalyst, CpHfCl₃/S1 (**5**). Reason for this is believed to be that after BuLi treatment carrier S3 contained more unreacted EtO-groups than carrier S1. These remaining ethoxy groups can have diminishing effect on catalyst activity.

The activity of heterogeneous CpHfCl₃/S1 (**5**) catalyst was only four times lower than that of homogeneous Cp₂HfCl₂ (**11**) catalyst. On this basis, a rather big proportion of the hafnium species on carrier was active in polymerization. This suggests that the structure of heterogeneous hafnium catalyst (**5**) was of the form Cp' CpHfCl₂ (structure A in Scheme 1), where Cp' is surface cyclopentadienyl group, which is attached to the carrier with trimethylene spacer. On the other hand, the chlorine analysis of catalyst **5** indicated that most of the hafnium species would be in inactive form as Cp' CpHfCl(O–Si≡) (structure B in Scheme 1). This means either that MAO cocatalyst was able to activate B type species or the chlorine analysis gave a too low value.

For supported η^5 -C₅(CH₃)₅ZrCl₃ and [η^5 -C₅(CH₃)₅]HfCl₃ the activity drastically decreased, for example, in the case of zirconium catalysts, the C₅(CH₃)₅ derivative (experiment 7a) was 40 times less active than the C₅H₅ derivative (experiment 4a). The activities of heterogeneous MCl₄(THF)₂ (M = Zr (**1**), Hf (**2**)) catalysts were low (*A* = 10 and 25 kg of PE/(mol M h), respectively).

Heterogeneous CpTiCl₃/S2 (**3**) catalyst exhibited low activity (*A* = 9 kg of PE/(mol of Ti h) at 60 °C) in ethylene polymerization. It was also thermally unstable, because lowering of polymerization temperature increased its activity (experiments 3a and 3b). Reason for the poor polymerization activity of titanium catalyst (**3**) is not clear. One explanation could be reduction of part of Ti(IV) species to Ti(III) species due to MAO cocatalyst, probably by TMA [37] in it. It is believed that Ti(III) species have only low activity in ethylene polymerization [37,38]. In the literature, studies [38–40] on CpMCl₃ and Cp₂MCl₂ complexes of titanium and zirconium prove (a) that titanium catalysts are readily reduced to the trivalent state by MAO, while (b) the zirconium catalysts have much higher stability against reduction. Moreover, (c) the amount of Ti(III) species in the reaction mixture is dependent on reaction conditions and the structure of the complex. Increase of temperature or Al/Ti mole ratio,

aging of the reaction mixture, or electronic deficiency of the titanium center promotes reduction of Ti(IV) species.

When we followed the consumption of ethylene, in experiments 3a (2700 ml), 3b (2300 ml), 4a (3300 ml), and 5a (3300 ml), the variation in activities of Ti (**3**), Zr (**4**) and Hf (**5**) catalysts towards ethylene was smaller than that observed on the basis of polyethylene yields. This led us to study the toluene phase after polymerization, and the GC tests proved that the titanium catalyst (**3**) produced butene, C₆–, C₈–, C₁₀–, and higher oligomers. It has been suggested, that weak donor ligands such as aromatic ethers can convert a polymerization catalyst into an oligomer producing catalyst system [41]. On this basis, in our polymerization experiments, the remaining Ti(IV) species were responsible for oligomerizing ethylene instead of polymerizing it due to the ethoxy groups and residual THF molecules on the carrier.

3.5. Polymer characterization

The molar mass distributions of polyethylenes produced in experiments 4a and 5a were narrow (*M_w/M_n* = 2.3) and indicate that there were only one type of active species present on the carrier in CpZrCl₃/S3 (**4**) and CpHfCl₃/S1 (**5**) catalysts. Molar masses (*M_w*) of polymers obtained with catalysts **4** and **5** were higher than those obtained with corresponding homogeneous catalysts **10** and **11**. For example, in experiment 5a (CpHfCl₃/S1 catalyst) the *M_w* was 504 000 g/mol, when in experiment 11a, with Cp₂HfCl₂ (**11**) catalyst, the *M_w* was lower (275 000 g/mol). Heterogeneous CpZrCl₃/S3 (**4**) catalyst produced polymer with a lower molar mass (*M_w* = 343 000 g/mol) than the corresponding hafnium catalyst. Polymer melting temperatures with catalysts **4**, **5**, **7**, and **8**, were between 135 and 139 °C, which belong to linear polyethylene [42]. Highest molar mass was obtained with ZrCl₄(THF)₂/S1 (**1**) catalyst and the *M_w* was 679 000 g/mol.

Lowest polyethylene melting points were obtained with heterogeneous titanium catalysts **3** and **6**, with broad melting range (catalyst **3**) or with two melting points (catalyst **6**) suggesting that these heterogeneous titanium catalysts contained different kinds of active sites. Furthermore, the molar mass distributions were very broad and bimodal for both of these

Table 5
Catalyst leaching study with CpZrCl₃/S3 (**4**) catalyst in ethylene polymerization^a

Catalyst	Experiment	Yield (g)	A ^b	T _m (°C)	M _w (g/mol)	M _w /M _n (g/mol)
CpZrCl ₃ /S3 (4)	a ^c	2.6	180	137.4	259000	3.0
Filtrate	b ^d	1.8		138.9	271000	2.7

^a Polymerization conditions: polymerization medium toluene (300 ml), ethylene overpressure of 2 bar, T_p = 60°C, t_p = 20 min.

^b Activity in kg of PE/(mol of Zrh).

^c Amount of catalyst 40 μmol. Cocatalyst 10 wt.% MAO, Al/Zr mole ratio 1000.

^d No additional cocatalyst used in the polymerization.

catalysts. In the bimodal molar mass distribution each maximum (which were partly overlapping) were handled separately. Thus, in Table 4, we announce two M_w values for each polymer sample of experiments 3a and 6a.

In the case of heterogeneous ZrCl₄(THF)₂/S1 (**1**), Cp*ZrCl₃/S3 (**7**) and Cp*HfCl₃/S1 (**8**) catalysts, the broad molar mass distributions of obtained polyethylenes suggested that there were different active sites on the carrier.

3.6. Catalyst treatment with MAO

Catalyst leaching was investigated by washing 110 mg of heterogeneous zirconium catalyst CpZrCl₃/S3 (**4**) with 10 wt.% MAO (Al/Zr = 1000) in toluene solvent at room temperature and separating the filtrate for polymerization test. In the polymerization with 110 mg of untreated CpZrCl₃/S4 (**4**) catalyst and with the Al/Zr mole ratio of 1000 (experiment a in Table 5) the yield of PE was 2.6 g. In the polymerization with the filtrate, no additional cocatalyst was added (experiment b). Because the filtrate showed activity in ethylene polymerization (PE yield was 1.8 g), MAO was able to desorb part of the catalyst to toluene phase.

In another experiment, heterogeneous CpZrCl₃/S catalyst was treated with MAO, so that the zirconium content of the remaining solid catalyst was analyzed. After treatment, the content of Zr was reduced to 4/5 of the original Zr content and the Al content of MAO treated heterogeneous CpZrCl₃/S catalyst was 11 wt.%. Our studies prove, that leaching is possible in catalysts, where the bonding of catalyst is based on chemical bond between the carrier and the catalyst.

4. Conclusions

Complexes of titanium, zirconium and hafnium were attached to the Cp-modified silica carrier with a help of *n*-BuLi. When Cp''MCl₃ (M = Ti, Zr, Hf, Cp'' = C₅H₅, C₅Me₅) were attached to the carrier bis(cyclopentadienyl) complexes were formed and when MCl₄(THF)₂ (M = Zr, Hf) complexes were attached to the carrier heterogeneous monocyclopentadienyl species were formed.

Characterization of the carrier materials before and after modifications with *n*-BuLi and metal complexes afforded important knowledge of how the modification had proceeded and offered some explanations to behavior of heterogeneous catalysts, too. The unreacted EtO-groups, originating from the silane coupling agent and possibly the residual THF molecules on the surface of carriers seemed to have diminishing effect on catalyst activity.

The activity and behavior of the resulting heterogeneous catalyst was affected by the metal and the complex type. For CpZrCl₃ or CpHfCl₃ immobilized on the cyclopentadienyl surface of the silica, high activities were obtained. Furthermore, the narrow molar mass distribution of the obtained polymers indicated, that the formed active sites were uniform.

The behavior of heterogeneous CpTiCl₃/S2 catalyst deviated from that of corresponding zirconium and hafnium catalysts. Its activity in ethylene polymerization was much lower and the molar mass distribution of polyethylene was very broad and bimodal. Additionally, the titanium catalyst dimerized and oligomerized ethylene, which was deduced to be due to the presence of THF and EtO-groups on the carrier. One reason for the low activity in polymerization was suggested to be the reduction of part of

the Ti(IV) species into Ti(III) species by MAO co-catalyst.

Activities of the heterogeneous $MCl_4(THF)_2$ ($M = Zr, Hf$) and Cp^*MCl_3 ($M = Ti, Zr, Hf$) catalysts were relatively low, and the broad molar mass distributions indicated that different kind of active species were formed on the carrier. However, the heterogeneous $HfCl_4(THF)_2/S2$ catalyst produced polymer with a narrow molar mass distribution.

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