

# Immobilization of $\text{CrCl}_3(\text{THF})_3$ on a cyclopentadienyl surface of silica

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## Abstract

Heterogeneous cyclopentadienylchromium catalysts were synthesized by adsorbing chromiumtrichloride  $\text{CrCl}_3(\text{THF})_3$  on a cyclopentadienyl modified silica surface. The obtained catalysts and the homogeneous model compound,  $[\text{CpCrMe}(\mu\text{-Cl})_2]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), were tested in the polymerization of ethylene with the presence of the methylaluminoxane (MAO) cocatalyst. The heterogeneous catalyst showed a good activity toward ethylene but the main products were oligomers, mainly *n*-butene. The homogeneous catalyst was a better polymerization catalyst but it also produced oligomers. Heterogeneous catalysts were characterized with FTIR and  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP MAS NMR. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Chromium; Silica; Ethylene; Polymerization; Heterogeneous catalyst

## 1. Introduction

Two types of chromium-based heterogeneous ethylene polymerization catalysts are commercially important: the Phillips catalyst (e.g.,  $\text{CrO}_3$  on  $\text{SiO}_2$ ) and the Union Carbide catalyst ( $\text{Cp}_2\text{Cr}$  on  $\text{SiO}_2$ ) [1]. Despite the industrial use and research, the chemical nature and oxidation state of the active site and the polymerization mechanism are not well known [2]. One reason to this has been the lack of homogeneous chromium model compounds that polymerize ethylene. The

first examples of well-characterized homogeneous model compounds are half-sandwich  $\text{Cp}^*\text{Cr(III)}$  systems ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) synthesized and tested in the polymerization of ethylene by Theopold's group [3]. On the basis of these experiments, they propose that the active site of the Union Carbide catalyst consists of a coordinatively unsaturated cyclopentadienylchromium(III) alkyl, for example  $[\text{Cp}^*\text{Cr(L)R}]^+$  and  $\text{Cp}^*\text{CrR}_2$ , which have a 13-electron configuration and a coordination number of five [1,3]. An example is  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+ \text{BPh}_4^-$  [4] complex, which can lose one of its THF molecules in solution and polymerize ethylene at room temperature and at atmospheric pressure without any added cocatalyst. An active complex in the polymerization is, hence,

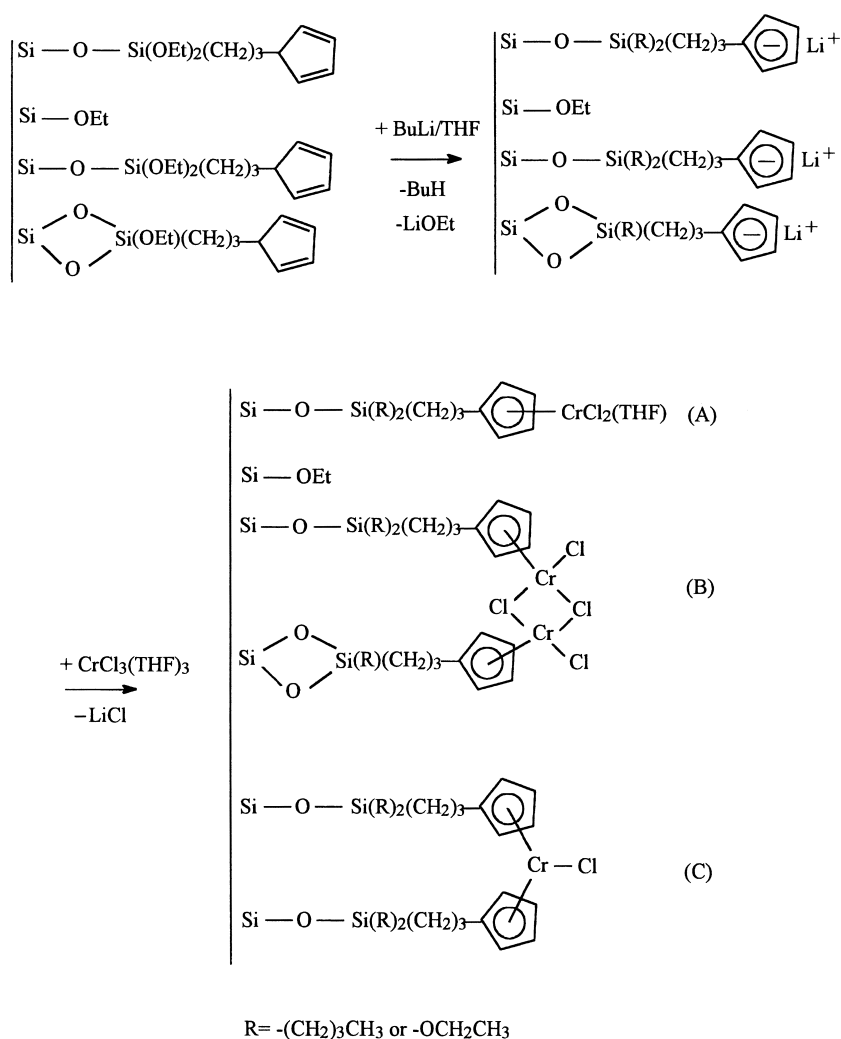
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five-coordinated  $[\text{Cp}^* \text{Cr}(\text{THF})\text{Me}]^+$  cation. The produced polyethylene has high density, narrow polydispersity, but relatively low molecular weight. An example of neutral complex is  $\text{Cp}^* \text{Cr}(\text{CH}_2\text{-SiMe}_3)_2$  [5]. At room temperature, it decomposes, but at low temperatures (below  $0^\circ\text{C}$ ), it produces a similar kind of polyethylene as  $[\text{Cp}^* \text{Cr}(\text{THF})_2\text{Me}]\text{BPh}_4$  catalyst [3].

The aim of this study was to prepare a new kind of heterogeneous polymerization catalyst, in which cyclopentadienylchromium species is

covalently bonded to the surface of silica. The surface of silica was first modified with a silane coupling agent,  $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ . Then the obtained cyclopentadienyl surface was used to construct a heterogeneous chromium catalyst by adsorbing  $\text{CrCl}_3(\text{THF})_3$  on the surface. In the formed catalyst, chromium is chemically bonded to the surface via the Cp ligands (Scheme 1). The prepared catalysts were tested in the polymerization of ethylene in the presence of methylaluminoxane (MAO). For comparison, a



Scheme 1. Preparation of heterogeneous cyclopentadienylchromium catalyst and its proposed structure. Most probable structures are the monocyclopentadienyl species (structure A) or the dimer (structure B).

homogeneous cyclopentadienylchromium(III) catalyst,  $[\text{CpCrMe}(\mu\text{-Cl})_2]$  [2], was also synthesized.

## 2. Experimental

### 2.1. Materials

All reactions and manipulations were carried out under inert nitrogen atmosphere by standard syringe or Schlenk techniques. Solvents, tetrahydrofuran, toluene, and *n*-pentane, were distilled over sodium-benzophenone ketyl before use. Silica (EP 10, Crosfield) with a surface area of 320 m<sup>2</sup>/g, a pore volume of 1.8 cm<sup>3</sup>/g, and a mean particle size of 100 μm was used as a support. The modified supports were prepared from silica, which was preheated at 600°C (S1) or at 820°C (S2) for 16 h in air.  $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{Cp}$  (ABCR) was used without further purification. CpLi (97%), MeLi (1.5 M in diethyl ether), and *n*-BuLi (2.5 M in hexane) were ordered from Aldrich. The cocatalyst MAO (10 and 30 wt.% MAO) was purchased from Witco. Ethylene (99.95%, AGA) was further purified by passing it through columns containing molecular sieves and Cu catalyst on a Al<sub>2</sub>O<sub>3</sub> carrier.

### 2.2. Synthesis of chromium complexes

$\text{CrCl}_3(\text{THF})_3$  was prepared according to the procedure described in the literature [6]. The C–O–C stretching frequencies of THF were observed at 854 cm<sup>-1</sup> (symmetric) and 1011 cm<sup>-1</sup> (asymmetric).  $[\text{CpCrMe}(\mu\text{-Cl})_2]$  was synthesized according to the literature procedure [2] from CpLi and  $\text{CrCl}_3(\text{THF})_3$  in THF. Calculated elemental analysis for C<sub>12</sub>H<sub>16</sub>Cl<sub>2</sub>Cr<sub>2</sub>: C, 43.00; H, 4.81. Found: C, 41.91; H, 4.62. Elemental analyses were conducted with Carlo Erba Instruments EA 1110 elemental analyzer.

### 2.3. Modification of silica

The modified silica carriers were prepared with atomic layer chemical vapor deposition (ALCVD) technique. In this technique, silica surface is modified with vaporized  $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$  at 280°C. Characteristics to this technique is that no solvents are used. The reaction conditions have been optimized, so the saturated gas–solid reactions produce modified materials with a uniform quality. A more detailed description of the technique and characterization of the modified carrier can be found in earlier publications of our laboratory [7,8]. The carbon contents of the modified silica carriers were 6.7 wt.% (S1) and 5.0 wt.% (S2). The estimated number of cyclopentadienyl groups on the silica surface were calculated from the carbon contents of the modified carriers assuming that silane is bonded to the surface of silica through one siloxane group. The <sup>29</sup>Si CP MAS NMR measurements of the modified carriers support this assumption (Figs. 3 and 4). The cyclopentadienyl group contents are 0.46 mmol for S1 and 0.35 mmol for S2 per 1 g of support material. This corresponds to 0.9 and 0.8 Cp/nm<sup>2</sup> for supports S1 and S2, respectively.

### 2.4. Preparation of the supported catalysts

#### 2.4.1. Catalyst no. 1

A solution of butyllithium (1.5 ml, 3.75 mmol) and THF (20 ml) was added into a suspension of modified silica S1 (1.0 g) at –30°C under vigorous stirring. The temperature of the reaction mixture was allowed to rise to room temperature and the mixture was then left overnight at room temperature. The solid part was separated by filtration and washed three times with THF. A THF (30 ml) solution of  $\text{CrCl}_3(\text{THF})_3$  (217 mg, 0.58 mmol) was added in small portions into the suspension of the obtained silica in THF at –75°C. And the temperature was again allowed to gradually rise to room temperature and the stirring was continued overnight. The final green solid was separated and washed with THF and pentane, and

then the solvent was removed under vacuum at room temperature.

#### 2.4.2. Catalyst no. 2

Catalyst no. 2 was prepared like catalyst no. 1 using support S2, but the amounts of *n*-butyllithium and  $\text{CrCl}_3(\text{THF})_3$ , when compared with the amount of Cp groups on the carrier, were smaller. In addition, *n*-BuLi and  $\text{CrCl}_3(\text{THF})_3$  were added to the reaction mixture at room temperature, and the reaction times after each addition was only 1 h. The final green catalyst was sealed in small portions into glass ampules under vacuum and the ampules were opened just before use in glove box. The chromium contents of the supported catalysts were determined with atomic adsorption spectrometer. The catalyst preparation and chromium analysis data are listed in Table 1. The catalysts were stored under nitrogen in a glove box.

#### 2.5. CP MAS NMR spectra

NMR measurements of the silica-based samples were carried out with a Bruker AMX-400 FT NMR spectrometer equipped with a magic angle spinning probehead. The samples were packed in glove box in  $\text{ZrO}_2$  rotors equipped with KEL-F caps. For the CP MAS NMR measurements, the solvents were removed from samples under vacuum at room temperature for prolonged times.  $^{13}\text{C}$  CP MAS NMR spectra were measured at 100.63 MHz, with a contact time of 3 ms and a delay of 4 s. In the  $^{29}\text{Si}$  CP MAS NMR (79.49 MHz) measurements, the contact time was 5 ms and the delay 5 s. Glycine  $(\text{NH}_2)\text{CH}_2\text{COOH}$  (C=O carbon res-

onating at 176.1 ppm) and adamantane ( $\text{C}_{10}\text{H}_{16}$ ) ( $\text{CH}_2$  carbons resonating at 38.3 ppm) were used as reference compounds in  $^{13}\text{C}$  NMR and octa(trimethylsilyl)octasiloxane  $[(\text{CH}_3)_3\text{Si}]_8\text{Si}_8\text{O}_{20}$  (the doublet resonances of  $\text{Si}(\text{CH}_3)_3$  silicons at 11.47 and 11.67 ppm) in  $^{29}\text{Si}$  NMR. The spinning rate for the 7 mm spinner was 4500 Hz. Number of transients was usually 16 000–20 000.

#### 2.6. FTIR spectra

The FTIR spectra of  $\text{CrCl}_3(\text{THF})_3$  and polymers were recorded with a Nicolet Magna 750 instrument. The samples were dispersed in dried KBr and pressed into discs. The supported catalysts and  $[\text{CpCrMe}(\mu\text{-Cl})_2]$  were characterized under nitrogen atmosphere by the Nicolet Impact 400 D FTIR spectrometer by the diffuse reflectance technique (DRIFT).  $[\text{CpCrMe}(\mu\text{-Cl})_2]$  was dispersed in dried KBr before measurement. The spectrometer was equipped with a mercury–cadmium–telluride (MCT) detector. The infrared spectra were recorded at a resolution of  $2\text{ cm}^{-1}$ .

#### 2.7. Polymerization procedure

The activities of the catalysts were tested by ethylene polymerization in toluene in a  $0.5\text{ dm}^3$  thermostated stainless steel reactor (Büchi) equipped with a magnetic stirrer (Büchi, BMA220). The catalyst and MAO were packed in containers in a glovebox and added into the evacuated reactor using a slight nitrogen overpressure. The total volume of polymerization medium was  $300\text{ cm}^3$ . Ethylene feeding was

Table 1  
Preparation and analysis of heterogeneous catalysts

Catalyst	Carrier	Cp content on carrier <sup>a</sup> (mmol/g)	$m_{\text{carrier}}$ (g)	Amount of BuLi (mmol)	Amount of $\text{CrCl}_3(\text{THF})_3$ (mmol)	[Cr] (wt.%)	Cp/Cr ratio <sup>a</sup> (mol/mol)
1	S1	0.46	1.0	3.8	0.58	1.96	1.2
2	S2	0.35	2.6	5.0	0.91	1.50	1.2

<sup>a</sup>Estimated value.

started at the polymerization temperature. The ethylene overpressure (2 bar) was adjusted and kept constant with a pressure meter/controller (Bronkhorst BP-602C). The total consumption of ethylene (consists of filling of the reactor and consumption during polymerization) was measured by 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. Degassing and adding of ethanol to the reactor stopped the polymerization. The mixture of polymer, ethanol, and hydrochlorid acid was stirred for 2 h. Then the precipitated polymer was filtered from the mixture, washed with ethanol and dried at 60°C overnight.

### 2.8. Polymer characterization

Melting temperatures ( $T_m$ ) were determined with a Mettler Toledo DSC821 differential scanning calorimeter. The melting endotherms were measured for samples that had previously been melted at 180°C and recrystallized, and the polymer sample was heated to 180°C at a rate of 10°C/min. Molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) with a Polymer Laboratories GPC210 device, equipped with two Polymer Laboratories MIXED A columns, an RI detector, and Precision Detectors 2040 laser light scattering (LS) detector. The samples were dissolved in 1,2,4-trichlorobenzene (TCB) and analyzed at 140°C with a flow rate of 1 ml/min. Calibration was carried out with a Polymer Laboratories PE standard ( $M_w = 119\,600$  and  $M_n = 100\,500$ ).

### 2.9. Gas chromatographic analyses

The oligomeric products of the polymerizations were determined with GC. After filtration of the polymer product from the reaction mixture, a sample of the organic liquid phase was separated and dried over molecular sieves (4 Å). The sample was then analyzed with GC. Gas

chromatographic analyses were performed on a HP 0.25-mm capillary column with a Hewlett Packard 6890 gas chromatograph equipped with a flame ionization detector (FID) and a Hewlett Packard 7683 integrator.

## 3. Results and discussion

### 3.1. Catalyst preparation

We have modified silica surface with a cyclopentadienyl silane compound,  $(\text{EtO})_3\text{-Si}(\text{CH}_2)_3\text{Cp}$ , which attaches to the surface of silica by reacting through its ethoxy groups with the surface silanol ( $\equiv\text{Si-OH}$ ) and siloxane ( $\equiv\text{Si-O-Si}\equiv$ ) groups [9]. The resulting modified silica has cyclopentadienyl surface, which is separated from the surface by a  $\text{CH}_2\text{CH}_2\text{CH}_2$  hydrocarbon spacer. The modification of the carrier is then continued in liquid phase so that the modified silica is treated with an excess of *n*-butyllithium, compared with the estimated amount of silane on the carrier, to convert the cyclopentadienyl groups into anions capable to bind the metal complex. The synthesis of the heterogeneous catalysts is presented in Scheme 1. Butyllithium also alkylates part of the remaining Si-OEt groups of the silane so that these groups are changed to Si-Bu groups. Finally,  $\text{CrCl}_3(\text{THF})_3$  complex is allowed to adsorb on the carrier. The unreacted chromium complex and formed LiCl is then washed from the synthesized heterogeneous catalyst.

The heterogeneous CpCr-catalysts were prepared in different ways so that the reaction times and temperatures were varied. In the preparation of catalyst no. 1, modified silica carrier was treated with a large excess of *n*-BuLi before adsorption of the  $\text{CrCl}_3(\text{THF})_3$  to alkylate all the Si-OEt groups present on the carrier and to prevent the reaction of chromium compound with Si-OEt groups. The reagents were added to the reaction mixture at lowered temperatures. The meaning was to try to prevent catalyst decomposition due to possible warming

up of the reaction mixture. Catalyst no. 2 was synthesized at room temperature and the reaction times were shortened to 1 h because we suspected that catalyst would decompose during a longer reaction. The synthesis of catalyst no. 2 thus resembles the synthesis of the reference compound,  $[\text{CpCrMe}(\mu\text{-Cl})_2]_2$ , which was synthesized at room temperature.

The chromium contents of catalyst nos. 1 and 2 are 1.96 and 1.50 wt.%, respectively. The lower amount of chromium in catalyst no. 2 depends on the lower silane content of the carrier S2 because before the silane treatment silica was preheated to higher temperature (820°C) than in the preparation of catalyst no. 1, where the preheating temperature was 600°C. The estimated mole ratio of cyclopentadienyl to chromium in both of these catalysts is 1.2 (Table 1).

### 3.2. Characterization of the catalysts

#### 3.2.1. MAS NMR spectra

The prepared heterogeneous chromium catalysts were characterized with  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP MAS NMR.  $^{13}\text{C}$  CP MAS NMR spectra of carrier S1, carrier after *n*-BuLi treatment, and catalyst no. 1 are in Fig. 1. The resonances of these spectra are reported in Table 2. In the spectrum of modified carrier, there are  $\text{CH}_3$  and  $\text{CH}_2$  carbons of the ethoxy groups of the silane coupling agent at 16 and 58 ppm, respectively. In addition, there are Si–OEt groups which are bonded directly to the surface of silica, these groups are formed in the reaction between ethoxy groups of silane and the surface siloxane bridges ( $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ ) [9]. The surface bound ethoxy groups cannot, however, be distinguished from the ethoxy groups connected to the silane because they have  $^{13}\text{C}$  NMR signals at the same position. The silane methylene groups of the  $\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cp}$  moiety resonate at 11, 21, and 33 ppm. The cyclopentadienyl methine carbon resonances at 42, 127, and 145 ppm are relatively broad and not clearly distinguishable.

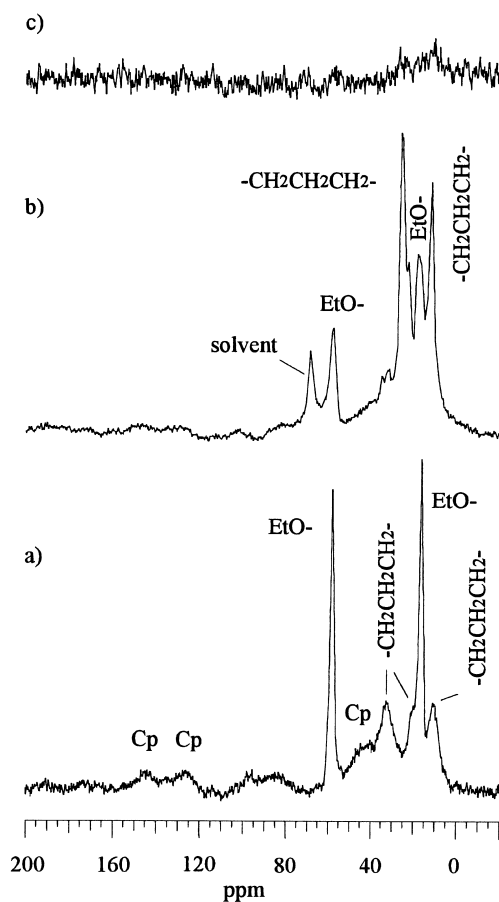


Fig. 1.  $^{13}\text{C}$  CP MAS NMR spectra of (a) carrier (S1), (b) carrier after BuLi treatment, and (c) catalyst no. 1.

In  $^{13}\text{C}$  NMR spectrum of the carrier after *n*-butyllithium treatment, some changes can be seen. The resonances of the ethoxy groups have diminished and the resonances originating from butyl groups and methylene carbons of  $\text{CH}_2-\text{CH}_2\text{CH}_2\text{Cp}$  moiety are overlapping in the chemical shift area of 11–33 ppm. A new resonance at 68.8 ppm belongs to residual solvent (the  $\text{CH}_2-\text{O}-\text{carbon}$  of THF). The  $\text{CH}_2-\text{CH}_2-\text{CH}_2$  carbon signal of THF at 26 ppm is overlapped. The resonances of the cyclopentadienyl anion are not distinguished so well possibly because the spin–spin coupling between lithium cation and the carbons broadens the resonances.

Table 2

<sup>13</sup>C Chemical shifts (δ) of the carriers (S1 and S2), carriers after BuLi treatment, and the heterogeneous catalysts

Sample	CH <sub>3</sub> –CH <sub>2</sub> –O–	Si–CH <sub>2</sub> –CH <sub>2</sub> –CH <sub>2</sub> –R(R=Cp or –CH <sub>3</sub> )	Cp
S1	15.9, 57.9	10.9, 20.6, 32.6	41, 127, 145
S2	15.9, 57.8	10.5, 21.3, 32.3	42, 126, 145
BuLi/S1	16.7(sh) <sup>a</sup> , 57.9	11.7, 18.1, 22.6(sh), 25.9, 31.6	40, 129, 147
BuLi/S2	16.9, 58.3	11.9, 18.3(sh), 22.3(sh), 25.5, 32.7	40, 125, 146
Cr/S1 (cat 1)	56	9.6, 26.3	not resolved
Cr/S2 (cat 2)	16.7, 58.7	11.8, 16.7, 25	not resolved

<sup>a</sup>Abbreviation sh means shoulder.

In the <sup>13</sup>C NMR spectrum of chromium catalyst no. 1, only two weak resonances can be distinguished at 10 and 26 ppm originating from butyl groups (Fig. 1). This is due to the paramagnetic nature of the chromium(III) species, which broadens the NMR resonances to such an extent that they have become unobservable. On the other hand, the spectra proves that chromium compound has adsorbed on silica surface and most probably on cyclopentadienyl groups. The spectrum of catalyst no. 2 (Fig. 2) resembles that of catalyst no. 1.

In the <sup>29</sup>Si CP MAS NMR spectrum (Fig. 3) of modified carrier S1 the resonances of the Si–OEt moieties at –53 and –58 ppm belong to silicon atoms of silane that are bound to the surface of silica with either one (monodentate form) or two (bidentate form) siloxane bonds, respectively (Table 3). Because the resonance at –53 ppm has a higher intensity than the resonance at –58 ppm (can be seen as a shoulder) the silane, Cp(CH<sub>2</sub>)<sub>3</sub>Si(OEt)<sub>3</sub>, has reacted with the surface mainly through one ethoxy group. The resonance at –110 ppm is due to siloxane bridges (≡Si–O–Si≡) of silica. The ≡Si–OH group silicons resonate at about –100 ppm [10], this resonance is not distinguishable in the carrier S1 spectrum, but the siloxane resonance is broadened, so there are some internal and possibly surface ≡Si–OH groups left in the carrier. The concentration of all the remaining ≡Si–OH groups is small when compared with the concentration of siloxane groups.

The <sup>29</sup>Si signal of ≡Si–OEt groups bonded directly to the surface of silica is not visible in

the carrier spectra. This signal should be close to –103 ppm where the signal of (EtO)Si(O–)<sub>3</sub> moiety of siloxanes has been reported to appear [13]. The signal of the surface bound ≡Si–OEt is possibly not distinguished because their amount is small in the carrier and because the

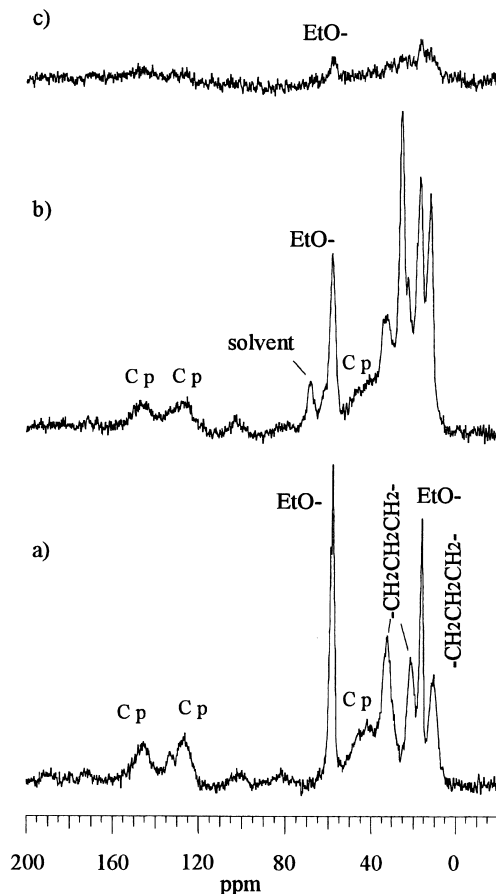


Fig. 2. <sup>13</sup>C CP MAS NMR spectra of (a) carrier (S2), (b) carrier after BuLi treatment, and (c) catalyst no. 2.

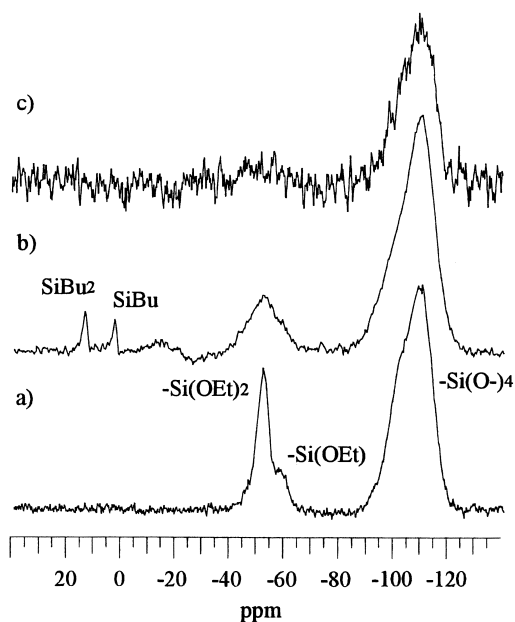


Fig. 3.  $^{29}\text{Si}$  CP MAS NMR spectra of (a) carrier (S1), (b) carrier after BuLi treatment, and (c) catalyst no. 1.

CP MAS NMR spectra is not quantitative. The intensity of the signals is proportional to the extent of cross polarization and, hence, depends on the distance between  $^{29}\text{Si}$  and  $^1\text{H}$  nuclei [14].

After butyllithium treatment (Fig. 3b) the silane resonances due to Si–OEt groups are smaller, but there are still ethoxy groups left in the carrier even though we used large excess of butyllithium in synthesis. The new resonances at 3 and 14 ppm belong to silane  $\equiv\text{Si}-\text{Bu}$  and  $=\text{Si}(\text{Bu})_2$  groups, respectively. In the spectrum of catalyst no. 1, the signal to noise ratio is poor because of the presence of paramagnetic

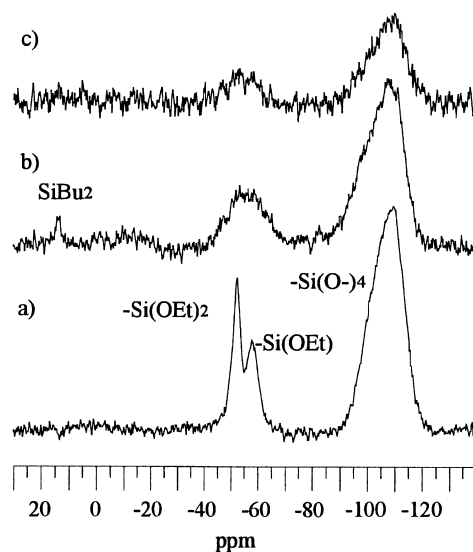


Fig. 4.  $^{29}\text{Si}$  CP MAS NMR spectra of (a) carrier (S2), (b) carrier after BuLi treatment, and (c) catalyst no. 2.

chromium and only the resonance due to siloxane bridges is observed at  $-109$  ppm (Fig. 3c). The  $^{29}\text{Si}$  CP MAS NMR spectra of carrier S2, the same carrier after BuLi treatment, and the corresponding catalyst no. 2 are presented in Fig. 4. In the spectrum of carrier S2, the resonance at  $-58$  ppm has higher intensity than the corresponding resonance in the spectrum of carrier S1 (Fig. 3a) indicating that concentration of the bidentate form of the silane has increased. After butyllithium treatment of the carrier S2, there is one resonance due to  $\text{Si}(\text{Bu})_2$  groups at  $13$  ppm visible (Fig. 4b).

There is no resonance of surface  $\text{BuSi}(\text{O}-)_3$  groups indicating that butyllithium has not alky-

Table 3

$^{29}\text{Si}$  chemical shifts of the carriers (S1 and S2), carriers after BuLi treatment, and the heterogeneous catalysts

Sample	Si–Bu	Si(Bu) <sub>2</sub>	Cp(CH <sub>2</sub> ) <sub>3</sub> (CH <sub>3</sub> CH <sub>2</sub> O) <sub>n</sub> Si(OSiO <sub>3</sub> ) <sub>3–n</sub>		Si(OSiO <sub>3</sub> ) <sub>4</sub>
			n = 2	n = 1	
S1	–	–	–52	–58	–110
S2	–	–	–53	–58	–110
BuLi/S1	3.0	14.2	–51	–	–110
BuLi/S2	–	13.1	–54	–	–107
Cr/S1 (cat 1)	–	–	–52	–	–109
Cr/S2 (cat 2)	–	–	–52	–	–110



lated the surface  $\text{EtOSi(O-)}_3$  groups. The signal of silicon that is bound to one alkyl group would resonate near  $-67$  ppm where the tridentate silane  $\text{RSi(O-)}_3$  [11] has been reported to appear.

### 3.2.2. FTIR spectra

The IR band of isolated  $\equiv\text{Si-OH}$  groups of silica at  $3741.5\text{ cm}^{-1}$  disappears when silica is treated with the silane (Fig. 5). A new broad band in the area  $3100\text{--}3700\text{ cm}^{-1}$  in the spectrum of modified silica (S1) is due to the hydroxyl groups of silica which are hydrogen bonded with oxygen atoms of the ethoxy groups of the silane. This band also contains the internal  $\equiv\text{Si-OH}$  (intraglobular) groups of the sil-

ica structure at  $3650\text{ cm}^{-1}$  [12], which are not able to react with silane coupling agent. Moreover, the modified carrier contains a weak band at  $3043\text{ cm}^{-1}$  [ $\nu(\text{CH})$ ], which belongs to the cyclopentadienyl group when it is  $\eta^1$ -bonded. When the carrier has been modified with BuLi and chromium is adsorbed on cyclopentadienyl groups the  $3043\text{ cm}^{-1}$  band diminishes, which indicates changes in the bonding mode of the cyclopentadienyl groups. Heterogeneous CpCr catalyst has the  $\nu(\text{CH})$  band due to Cp ligand probably near  $3100\text{ cm}^{-1}$  where the  $\text{CpCrCl}_2$  has its  $\nu(\text{CH})$  stretching [15], but the band is not well distinguished. The FTIR spectra of unmodified silica, carrier S1, the same carrier after butyllithium treatment and the heterogeneous catalyst no. 1 are presented in Fig. 5. Otherwise, there are no big differences between the carrier and the catalyst spectra because the strong bands of silica practically cover the bands due to catalyst. The  $\nu(\text{CH})$  stretchings of the methylene ( $\text{CH}_2$ ) and methyl ( $\text{CH}_3$ ) groups are below  $3000\text{ cm}^{-1}$ . The FTIR spectra of carrier S2 and catalyst no. 2 are presented in Fig. 6 and resemble those of carrier S1 and catalyst no. 1.

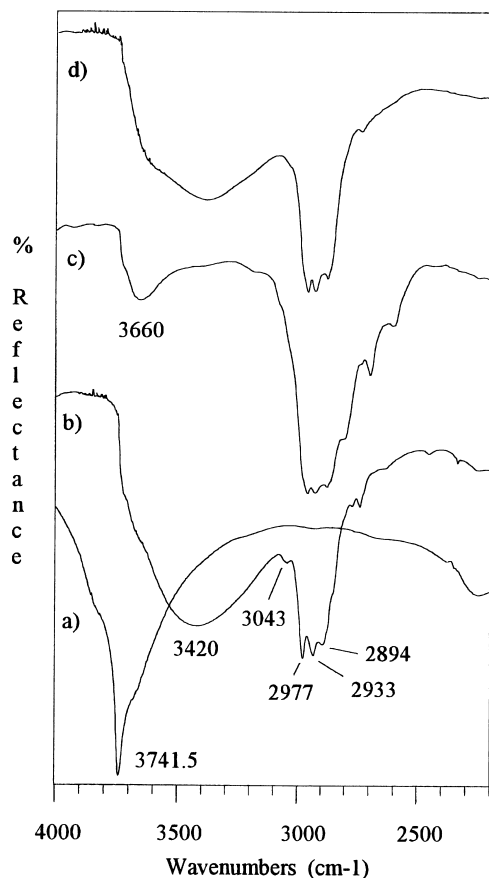


Fig. 5. FTIR spectra of (a) unmodified silica, (b) modified silica carrier (S1), (c) modified silica carrier after BuLi treatment, and (d) catalyst no. 1.

### 3.3. Catalyst structure

Silica was modified by atomic layer chemical vapor deposition (ALCVD) technique. The advantage in this kind of preparation is that the coupling agent is chemically bonded to the support and solvent effects can be eliminated. When, in addition, chromium compound is chemically bonded to the surface, the catalyst has smaller possibilities to leach from the carrier during the polymerization.

A proposed structure of the prepared heterogeneous cyclopentadienylchromium catalyst is of the form  $\text{CpCr(III)Cl}_2(\text{THF})$ , which is presented in Scheme 1 as structure A. Thus, we would have a heterogeneous catalyst with 15 valence electrons and a coordination number of six. This chromium(III) compound is also paramagnetic because it has three unpaired electrons. If the complex loses its THF ligand (for

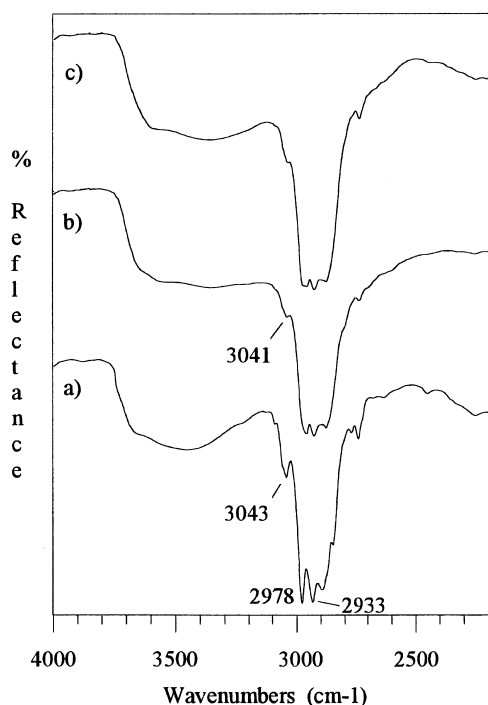


Fig. 6. FTIR spectra of (a) modified silica carrier (S2), (b) modified silica carrier after BuLi treatment, and (c) catalyst no. 2.

example, in vacuum) it possibly forms dimers, because trivalent chromium avoids unsaturation by forming dimers so that chromium gains six-coordination [5] (see structure B). The prepared heterogeneous cyclopentadienylchromium catalyst is green like the  $\text{CpCrCl}_2$  complex [15].

Some chromium atoms are possibly bound to two cyclopentadienyl groups (structure C) because there are more cyclopentadienyl groups than chromium atoms present on the carrier (the estimated mole ratio of cyclopentadienyl to chromium is 1.2). The chromium fragment containing two cyclopentadienyl ligands has a coordination number of at least six, and therefore, it would not be very good polymerization catalyst because Theopold considers six-coordinated complexes to be coordinatively saturated [3]. However, chromocene,  $\text{Cp}_2\text{Cr}$ , and  $\text{Cp}_2\text{CrI}$  have been reported to produce some polymer in the presence aluminium alkyl under high pressure [16]. Chromiumtrichloride can, in addition to Cp groups, also react with the remaining Si—OEt

groups on the silica. So there are different ways how chromium can be bonded to the present silica surface.

### 3.4. Polymerization

The prepared chromium catalysts were activated with MAO, the function of which, in the case of metallocene catalysts, is to alkylate the complex and to abstract an anion from the complex and thus generate an active cationic 14-electron species,  $[(\text{Cp}_2\text{MMe})^+]$ , which is associated with the MAO-derived anion [17]. The same type of reaction probably takes place in the case of chromium, too. Theopold's group has not examined reactions between  $\text{Cp}^*\text{Cr}$  compounds and MAO [3], but there are some examples where MAO has been used to activate these catalysts, for example,  $[\text{CpCrMe}(\mu\text{-Cl})]/\text{MAO}$  [2] and  $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2/\text{MAO}$  [18] catalyst systems.

The polymerization results are presented in Table 4. The polymerization activities of the heterogeneous catalysts remain relatively modest (between 4–11 kg of PE/(mol of  $\text{Cr}^x\text{h}$ )), when the results are compared with the activity of a corresponding homogeneous compound  $[\text{CpCrMe}(\mu\text{-Cl})]_2$  (catalyst no. 3). Catalyst nos. 1 and 2 were prepared in different ways, so that the amount of BuLi, reaction temperature, and reaction times were varied. Catalysts were, in addition, tested at different polymerization temperatures and with different mole ratios of Al to Cr. Changing the synthesis method or polymerization conditions did not, however, have any big influence on the polymerization activities of catalyst nos. 1 and 2. The amount of produced polyethylene does not, however, tell the whole truth of the activities of these catalysts if we consider the total amount of ethylene consumed during the polymerization (Table 4).

On the basis of ethylene consumption, we expected better polymerization activities for the heterogeneous catalyst than those reported. The total consumption of ethylene also contains the

Table 4

Polymerization of ethylene with heterogeneous catalysts and homogeneous  $[\text{CpCrMe}(\mu\text{-Cl})_2]$  catalyst<sup>a</sup>

Catalyst number	[Cr] (wt.%)	Run	Amount of catalyst (mg)	$n(\text{Cr})$ [ $\times 10^{-5}$ mol]	Al/Cr mole ratio	$T$ (°C)	Yield (g)	$T_m$ (°C)	$A^b$	Total consumption of ethylene (ml) at NTP
(1)	1.96	a	70	2.6	2300	40	0.23	133.2	6.0	1770
		b	70	2.6	2300	20	0.37	135.1	11.4	1930
(2)	1.50	a	237	6.8	700	15	0.59	122, 131.9	4.8	2910
		b	139	4.0	700	0	0.30	121, 133.5	4.0	2340
		c	107	3.1	1100	40	0.28		5.4	2790
(3) $[\text{CpCrMe}(\mu\text{-Cl})_2]$		a	11.4	6.8	1000	15	1.90	87, 125.4	28.1	5500
		b	14.0	8.3	500	15	1.94	85, 122.2	23.4	5360
		c	6.4	3.8	250	30	1.16		30.6	3200
Background <sup>c</sup>			–	–	–	30	–	–	–	1600

<sup>a</sup>Polymerization time 60 min. Ethylene overpressure 2 bar. Cocatalyst: 30 wt.% MAO for catalyst nos. 1 and 3; 10 wt.% MAO for catalyst no. 2. Stirring speed: 200 rpm for runs 1a–b; 400 rpm for runs 2–3.

<sup>b</sup>Activities in kg of PE/(mol of Cr<sup>x</sup>h). The amount of heterogeneous catalyst was subtracted from the yield, when the activities were calculated.

<sup>c</sup>Background experiment was conducted without any chromium catalyst, only 10 ml of 10 wt.% MAO was added to reactor. Reaction time was 30 min.

filling of the reactor to the desired pressure, which is about 1600 ml of ethylene at 30°C. This amount was deduced from the background experiment which was conducted without any chromium catalyst (see Table 4). In this run, no polymer was found in the reactor. For example, in run 2a, the ethylene consumption during the reaction after filling of the reactor is about 1000 ml and the yield should have been at least 1 g of polyethylene. When the ethylene consumption in different runs was compared, catalyst no. 2 was found more active than catalyst no. 1. One explanation for different activities of these two catalysts is probable in the air-sensitivity of the catalysts; catalyst no. 2 was better protected from contamination (synthesis time was markedly shorter and catalyst was stored in glass ampules). A noteworthy aspect with catalyst nos. 2 and 3 was that they both retained some activity (except in run 2b at 0°C) till the end of the polymerization because some ethylene was consumed even in the end of the polymerization experiments, too.

Moreover, the ethylene consumption in homogeneous polymerization promised higher polymer yields than those reported in Table 4. The highest consumption was registered in run

3a (5500 ml) where the yield of polyethylene was 1.90 g. Nevertheless,  $[\text{CpCrMe}(\mu\text{-Cl})_2]/\text{MAO}$  catalyst was a markedly better polymerization catalyst than the prepared heterogeneous catalysts. Because the polymer yields with catalysts 2 and 3 were smaller than one would expect from the ethylene consumption the toluene phase was examined with gas chromatography for the presence of oligomers.

### 3.5. Polymer characterization

#### 3.5.1. GC analyses

In polymerization experiments 2a, 3b, and 3c, the toluene phase was separated after the polymer filtration and analyzed with GC. The gas chromatographic analyses revealed that both the heterogeneous catalyst and the homogeneous catalyst oligomerize ethylene. The GC sample contained *n*-butene and other  $\text{C}_6^-$ ,  $\text{C}_8^-$ ,  $\text{C}_{10}^-$ ,  $\text{C}_{12}^-$ ,  $\text{C}_{14}^-$ ,  $\text{C}_{16}^-$  and higher oligomers. The main oligomerization product in the liquid phase was, however, *n*-butene.

#### 3.5.2. GPC analyses

Polyethylene samples from runs 2a and 3b were analyzed with GPC. The homogeneous

catalyst,  $[\text{CpCrMe}(\mu\text{-Cl})_2]/\text{MAO}$ , produced polyethylene with a very broad molecular weight distribution and low molecular weight. Practically the entire polymer had molecular weight that was below detection limit of the LS detector (about 30 000 g/mol), but there was a small fraction of polymer with higher molecular weight, too. The heterogeneous catalyst no. 2 produced polyethylene with  $M_w = 945\,000$ , but the molecular weight distribution was bimodal and broad ( $M_w/M_n = 11.2$ ).

$\beta$ -Hydrogen transfer partly explains why the prepared heterogeneous CpCr-catalysts had so low activity in the polymerization. In this reaction, a hydrogen from  $\sigma$ -bonded alkyl ligand or polymer chain is transferred to the chromium atom ( $\beta$ -H elimination) or to the monomer, and an alkene (e.g., butene or oligomer) is released [19]. However, according to Theopold,  $\beta$ -hydride elimination is not typical for trivalent  $\text{Cp}^*\text{Cr(III)}$  alkyl catalysts, but it is typical for divalent chromium alkyls that either produce oligomers or do not react with ethylene at all [3]. In our case, however, both the heterogeneous catalyst no. 2 and the homogeneous  $[\text{CpCr(III)Me}(\mu\text{-Cl})_2]/\text{MAO}$  catalyst produced oligomers, so the previous observation does not help in deducing the oxidation state of the prepared heterogeneous catalyst.

### 3.5.3. DSC

Measured melting points of the synthesized polymers support the GPC results. The melting range was broad and for polymers prepared with catalyst nos. 2 and 3 the polymer had two melting points.

Other explanations to low activities in the polymerization, in addition to  $\beta$ -hydrogen transfer, could be the sensitivity of the chromium catalysts to air and moisture. The homogeneous model compound,  $[\text{CpCrMe}(\mu\text{-Cl})_2]$ , changed rapidly its red color upon exposure to any contamination. The heterogeneous catalysts did not, however, change their color during storage under nitrogen in a glove box. Moreover, THF can be a catalyst poison, as it blocks the empty

coordination sites of the active catalyst. We have noticed that it is difficult to remove THF entirely from the heterogeneous catalysts. In addition, the chosen cocatalyst can have some influence on the performance of the prepared heterogeneous catalysts. However, other cocatalysts were not tested in the polymerization with the prepared catalysts. The polymerization conditions (e.g., catalyst concentration, appropriate solvent, temperature) were neither optimized.

Substitution of the cyclopentadienyl ligands would probably stabilize the complexes and enhance the activities of the prepared CpCr-catalysts. When different  $[\text{Cp}'\text{CrMeCl}]_2$  [2] complexes ( $\text{Cp}' =$  cyclopentadienyl derivative) were compared in the polymerization of norbornene, pentamethylcyclopentadienyl,  $\text{Cp}^*\text{Cr}$ , derivative of chromium produced considerably more polymer than corresponding CpCr derivative. Similar results were obtained with  $\text{Cp}'\text{Cr}(\text{acac})\text{Cl}$  ( $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ , acac = acetylacetonate) [20] complexes in the polymerization of ethylene.

### 3.5.4. IR

The prepared polymers were identified with IR spectroscopy. According to these spectra the polyethylene which is produced with heterogeneous catalysts is linear. Three doublets that belong to linear PE could be detected in the spectra (bands at 719, 730, 1463, 1474, 2849, and 2921  $\text{cm}^{-1}$ ). In the IR spectrum of polyethylene that was synthesized with homogeneous catalyst, there are, in addition to bands mentioned above, bands at 909 and 990  $\text{cm}^{-1}$  that belong to terminal vinyl groups ( $\text{CH}_2=\text{CH}-$ ), and a small band at 1379  $\text{cm}^{-1}$  arising from terminal methyl groups indicating some branching.

## 4. Conclusions

New kind of heterogeneous chromium catalyst was synthesized by immobilizing chromium chloride complex on a cyclopentadienyl surface.

In this catalyst, chromium is chemically bound to the Cp groups of the surface. Prepared heterogeneous catalyst was modest in the polymerization of ethylene when activated with MAO, but promising catalyst in the oligomerization of ethylene, which was proven by *n*-butene and other oligomers found from the polymerization medium. GPC analyses revealed that the produced polymers had broad molecular weight distribution and melting range.

Substitution of the cyclopentadienyl ligands would probably enhance the activities of the catalysts. In addition, the chosen polymerization conditions (e.g., temperature, cocatalyst) can have some influence on the performance of the catalysts. Both the paramagnetic nature of the chromium cyclopentadienyl compounds and air-sensitivity make the research of these chromium compounds challenging.

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## References

- [1] K.H. Theopold, CHEMTECH (1997) 26.
- [2] U. Peucker, W. Heitz, Macromol. Rapid Commun. 19 (1998) 159.
- [3] K.H. Theopold, Eur. J. Inorg. Chem. (1998) 15.
- [4] B.J. Thomas, S.K. Noh, G.K. Schulte, S.C. Sendlinger, K.H. Theopold, J. Am. Chem. Soc. 113 (1991) 893.
- [5] R.A. Heintz, S. Leelasubcharoen, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, Organometallics 17 (1998) 5477.
- [6] H.F. Holtzlaw, Inorg. Synth. 8 (1966) 150.
- [7] E.I. Iiskola, S. Timonen, T. Pakkanen, O. Härkki, P. Lehmus, J.V. Seppälä, Macromolecules 30 (1997) 2853.
- [8] E.I. Iiskola, S. Timonen, T.T. Pakkanen, O. Härkki, J.V. Seppälä, Appl. Surf. Sci. 121/122 (1997) 372.
- [9] J. Blümel, J. Am. Chem. Soc. 117 (1995) 2112.
- [10] E.F. Vansant, P. Van Der Voort, K.C. Vrancken, in: B. Delmon, J.T. Yates (Eds.), Characterization and Chemical Modification of the Silica Surface, Studies in Surface Science and Catalysis Vol. 93 Elsevier, Amsterdam, 1995, p. 61.
- [11] E.F. Vansant, P. Van Der Voort, K.C. Vrancken, in: B. Delmon, J.T. Yates (Eds.), Characterization and Chemical Modification of the Silica Surface, Studies in Surface Science and Catalysis Vol. 93 Elsevier, Amsterdam, 1995, p. 232.
- [12] E.F. Vansant, P. Van Der Voort, K.C. Vrancken, in: B. Delmon, J.T. Yates (Eds.), Characterization and Chemical Modification of the Silica Surface, Studies in Surface Science and Catalysis Vol. 93 Elsevier, Amsterdam, 1995, p. 66.
- [13] H. Marsmann, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), NMR, Basic Principles and Progress, Oxygen-17 and Silicon-29 Vol. 17 Springer-Verlag, Berlin, 1981, p. 187.
- [14] G. Engelhardt, H. Kohler, in: P. Diehl, E. Fluck, H. Günther, R. Kosfeld, J. Seelig (Eds.), NMR Basic Principles and Progress Vol. 31 Springer-Verlag, Berlin, Heidelberg, 1994, p. 18.
- [15] M. Morán, Transition Met. Chem. 6 (1981) 173.
- [16] Y. Tajima, K. Tani, S. Yuguchi, J. Polym. Sci., Part B: Polym. Lett. 3 (1965) 529.
- [17] F. Ciardelli, A. Altomare, M. Michelotti, Catal. Today 41 (1998) 149.
- [18] R. Emrich, O. Heinemann, P.W. Jolly, C. Krüger, G. Verhovnik, Organometallics 16 (1997) 1511.
- [19] C. Janiak, in: A. Togni, R.L. Halterman (Eds.), Metallocenes: Synthesis, Reactivity, Applications Vol. 2 Wiley-VCH, Weinheim, 1998, p. 563.
- [20] O. Heinemann, P.W. Jolly, C. Krüger, G.P.J. Verhovnik, J. Organomet. Chem. 553 (1998) 477.