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Immobilization of zirconium amide on a Cp-modified silica surface and its use as a catalyst for ethylene polymerization

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Abstract

Heterogeneous ethylene polymerization catalysts were prepared by supporting tetrakis(dimethylamino)zirconium on chemically modified silica surface. The silica was modified with a silane coupling agent, $Cp(CH_2)_3Si(OEt)_3$, using ALCVD-technique. On the resulting cyclopentadienyl surface zirconium amide, $Zr(NMe_2)_4$, was immobilized with and without using methyllithium. Depending on the use of methyllithium the immobilization resulted in either mono- or bis-cyclopentadienyl zirconium complexes, which were characterized using chemical analysis, FT-IR, ^{13}C- and ^{29}Si-NMR results. Moreover, a homogeneous model compound, $(Me_3SiCp)_2Zr(NMe_2)_2$, was synthesized with a reaction between $Zr(NMe_2)_4$ and Me_3SiCp. The preliminary results of ethylene polymerization with these supported and unsupported organometallic complexes are presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Metal amide; Silica; Ethylene; Polymerization

1. Introduction

Since the catalytic properties of metallocenes in olefin polymerization were discovered [1], a lot of effort has been expended to develop new catalysts for practical use. The metallocene compounds have been intensively studied, $EtInd_2ZrCl_2$ [2] being one of the most widely investigated, due to their high effect on (co)polymer microstructure and molecular weight. The metallocene dichloro complexes are difficult to prepare and yields are generally moderately low. Therefore recently there have been reports that the transition metal amide complexes of the type, $M(NR_2)_4$, are excellent precursors for the synthesis of *ansa*-metallocenes and bridged half-sandwich complexes [3].

In practice, modern industrial polymerization processes require a heterogeneous catalysts and in the last few years a number of studies have been devoted to the heterogenization of metallocene catalysts by supporting metallocene complexes on either inorganic or organic carriers [4]. The silica-supported catalysts are generally less active in polymerization of ethylene than their homogeneous counterparts, but the activity can be improved by modifying the silica support [5].

In this paper we report preparation of supported metallocene amide complexes that are active catalysts in ethylene polymerization. The monocyclopentadienyl zirconium amide catalyst has been prepared by a convenient amine elimination reaction between cyclopentadienyl modified silica surface and tetrakis(dimethylamino)zirconium. An analogous heterogeneous bis-cyclopentadienyl zirconium amide complex has been prepared in the reaction between methyllithium treated cyclopentadienyl surface and zirconium amide complex. As a homogeneous model for the heterogeneous systems a metallocene amide compound $(Me_3SiCp)_2Zr(NMe_2)_2$ has been synthesized and the ethylene polymerization activities of supported and unsupported systems will be presented.

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2. Experimental

2.1. General procedures

All the reactions were carried out under nitrogen atmosphere using the glovebox and Schlenk techniques. Silica (EP 10, Crosfield Ltd.) with a surface area of 320 m^2 g^{-1}, pore volume of 1.8 cm^3 g^{-1}, and mean particle size of 100 μm was used as a support. The surface modification of silica was carried out by using the saturated gas–solid reaction of a silane coupling agent, $Cp(CH_2)_3Si(OEt)_3$, and a partially dehydroxylated silica as described previously [5a]. Solvents, diethyl ether, hexane and toluene, were dried and deoxygenated by distillation over sodium with benzophenone as an indicator. $Zr(NMe_2)_4$ (Strem Chem.) and $CpSiMe_3$ (97%, Fluka) were used in synthesis without further purification. Methylaluminoxane (10 and 30% MAO in toluene) was purchased from Witco GmbH. Ethylene (AGA, grade 3.5) was passed through a purification system containing molecular sieves and activated Cu just before feeding to the reactor.

2.2. Characterization of catalysts

IR spectra were recorded with a Nicolet Impact 400D spectrometer equipped with a diffuse reflectance accessory and connected airtightly to a glovebox. The samples were measured under a nitrogen atmosphere as loosely packed powders with a 2 cm^{-1} spectral resolution. NMR measurements were carried out with a Bruker AMX 400 standard bore, high resolution NMR spectrometer equipped with a multinuclear magic-angle spinning probehead. ^{29}Si-CPMAS-NMR spectra were recorded at 79.5 MHz with a 5 ms contact time, a 5 s delay and 15 000 transients. ^{13}C-CPMAS-NMR spectra were obtained at 100.6 MHz with a 3 ms contact time, a 4 s delay and 20 000 transients. All NMR experiments were carried out using a spinning speed of 4.5 kHz. Elemental analysis for carbon, hydrogen and nitrogen were determined by Carlo Erba Instruments EA 1110 CHNS-O analyzer. Zirconium analyses were carried out with inductively coupled plasma atomic emission spectrometer (ICP).

2.3. Polymer analysis

Melting temperatures of the polyethylenes were measured with a Mettler Toledo Star DSC 821 system. The analyzed samples were in a powder form. The samples were heated first at a heating rate of 20°C min^{-1}, cooled and melted again at the heating rate of 10°C min^{-1}, and the second heating curve was analyzed. Molecular weights and molecular weight distributions of the polyethylene samples were determined using a Polymer Laboratories GPC210 instrument equipped with two Polymer Laboratories MIXED A columns and RI- and Precision Detectors 2040 (light scattering) detectors. The solvent, 1,2,4-trichlorobenzene, was applied at a flow rate of 1.0 ml min^{-1}. The calibration was made by using Polymer Laboratories PE standard with a narrow molecular weight distribution and Dowlex 2045 standard.

2.4. Modification of the silica support

SiO_2 was preheated at 600°C (S1) or 820°C (S2) for 16 h in air. The saturated gas–solid reaction was carried out in a commercial F-120 ALCVD (atomic layer chemical vapor deposition) reactor. Preheated silica was reacted with $(EtO)_3Si(CH_2)_3Cp$ at 280°C (S2) under nitrogen flow for 2 h. Carbon analysis found for materials: S1, 6.7; S2, 5.0%. ^{13}C-CPMAS-NMR: δ 10 (CH_2), 16 (OCH_2CH_3), 21 (CH_2), 33 (CH_2), 58 ($\mathbf{O}CH_2CH_3$), 42 (Cp), 126 (Cp) and 146 (Cp) ppm. ^{29}Si-CPMAS-NMR: δ − 108 (silica), − 58 ($RCH_2(OEt)\mathbf{Si}(OSiO_3)_2$) and − 52 ($RCH_2(OEt)_2\mathbf{Si}(OSiO_3)$) ppm.

2.5. Reaction of $Zr(NMe_2)_4$ with support S1

The hexane solution of $Zr(NMe_2)_4$ (0.12 ml, 0.5 mmol) was added dropwise to the hexane suspension of the modified silica. The mixture was refluxed for 6 h. The solid part was separated and washed three times with hexane and dried under vacuum at 40°C. Elemental analysis found for material: N, 1.58; Zr, 4.01; C, 8.28%. ^{13}C-CPMAS-NMR: δ 12 (CH_2), 18 ($OCH_2\mathbf{C}H_3$), 22 (CH_2), 32 (CH_2), 35 ($SiNMe_2$), 43 ($ZrNMe_2$), 58 ($\mathbf{O}CH_2CH_3$), 64 (ZrOEt), 129 (Cp) and 144 (Cp) ppm. ^{29}Si-CPMAS-NMR: δ − 109 (silica), − 58 ($RCH_2(OEt)\mathbf{Si}(OSiO_3)_2$), − 51 ($RCH_2(OEt)_2\mathbf{Si}(OSiO_3)_1$) and −39 ($RCH_2(OEt)(NMe_2)\mathbf{Si}(OSiO_3)$) ppm.

2.6. Reaction of MeLi with support S2

Into the suspension of modified silica in diethyl ether was added excess of methyllithium (1.6 M in diethyl ether). The mixture was stirred at r.t. overnight. The solid part was separated and washed three times with diethyl ether and dried under vacuum.

2.7. Reaction of $Zr(NMe_2)_4$ with MeLi treated support S2

Into the suspension of methyllithium treated modified silica in hexane was added excess of $Zr(NMe_2)_4$ in hexane. The mixture was refluxed for 3 h and stirred overnight. The solid material was separated and washed three times with hexane and dried under vacuum at 45°C. The elemental analysis found for material: N, 0.45; Zr, 1.58; C, 7.21%.

2.8. $(Me_3SiCp)_2Zr(NMe_2)_2$

A toluene solution of Me_3SiCp (0.6 ml, 3.6 mmol) was added dropwise to a toluene solution of $Zr(NMe_2)_4$ (0.3 g, 1.1 mmol) at -77°C. The mixture was stirred meanwhile the temperature was allowed to attain r.t. The mixture was heated to 60°C while a yellow color started to form and intensify. After the mixture was stirred overnight, the solvent was evaporated yielding a yellow solid. Elemental analysis calculated for $C_{20}H_{38}N_2Si_2Zr$: C, 52.92; H, 8.44; N, 6.17. Found: C, 53.2; H, 9.80; N, 5.13%. ^{1}H-NMR (toluene-d_8): δ 0.22 (s, $SiMe_3$), 2.84 (s, NMe_2), 6.19 (Cp) and 6.35 (Cp) ppm. ^{13}C-{^{1}H}-NMR (toluene-d_8): δ 0.21 ($SiMe_3$), 50.3 (NMe_2), 113.7 (Cp), 115.0 (Cp) and 120.0 (Cp). ^{29}Si (toluene-d_8): δ -8.44 (s) ppm.

2.9. Polymerization of ethylene

Ethylene was polymerized in a 0.5 dm^3 stainless steel autoclave. The catalyst suspended in toluene and MAO as a co-catalyst were placed into the reactor batchwise under nitrogen flow. Toluene as a reaction media was introduced into the reactor in a nitrogen flow. The amount of MAO used in the polymerization corresponded to the Al/Zr molar ratio of 1000 or 4000. The mixture was stirred and ethylene was led into the reactor at 2.5 bar pressure for half an hour at 80°C. The resulting polymer was poured into acidic ethanol, filtered and dried in an oven at 60°C.

3. Results and discussion

3.1. Preparation of the supported catalysts

The surface modification of silica was carried out by using a saturated gas–solid reaction of a silane coupling agent $Cp(CH_2)_3Si(OEt)_3$ with a partially dehydroxylated silica in an ALCVD reactor. In contrast to traditional silica modification methods reported in literature [5d] the modification of silica with ALCVD technique is uncomplicated and the possible solvent effects have been eliminated. The silica had been preheated at 600 (support S1) or 820°C (support S2) and after the modification reaction the carbon contents of support were 6.7 w% corresponding to 0.9 Cp nm^{-2} or 5 w% corresponding to 0.6 Cp nm^{-2}, respectively. The presence of cyclopentadienyl alkoxysilane on the silica surface was observed using ^{13}C- and ^{29}Si-CPMAS NMR spectroscopy and diffuse reflectance IR spectroscopy. The silane is bound to the silica surface with one and two siloxane bonds and the cyclopentadienyl group is separated from the silicon atom with a hydrocarbon spacer, $-(CH_2)_3-$ as described in Ref. [5a].

Tetrakis(dimethylamino)zirconium was attached to the cyclopentadienyl functionalized silica surface (S1) with a liquid phase reaction in hexane. The reaction between cyclopentadienyl and metal chloride is usually done in THF and with the help of alkyl lithium reagent. The reaction between metal amide and cyclopentadienyl does not require the use of an organolithium compound and therefore one step in catalyst preparation and the inconvenience due to the co-ordination of THF have been eliminated. The zirconium content of catalyst 1 was 4.01 w%, corresponding to the Zr loading of ca. 0.4 mmol g^{-1} or 0.8 atoms nm^{-2} of support which denotes Cp:Zr ratio of 1.1. The nitrogen contents of the catalyst was 1.58 w% which denotes N:Zr ratio of 2.6 indicating that zirconium is co-ordinated to one surface cyclopentadienyl yielding monocyclopentadienyltriaminozirconium surface groups (Fig. 1).

The ^{13}C-NMR spectrum of catalyst 1 showed three new signals (Fig. 2). The signal at chemical shift of δ 35 and 43 ppm are assigned to methyl groups of amine. The lower field signal at δ 43 ppm is assigned to the carbon of dimethylamine that is coordinated to zirconium and the higher field signal at δ 35 ppm is due to the carbon of the dimethylamine that is bonded to silicon of the silane [6]. The eliminated dimethylamine, $HNMe_2$, could react with the ethoxy groups bound to silicon of the coupling agent or there could be an exchange reaction between the ethoxy and amide groups yielding silicon–nitrogen bond and zirconium alkoxy group (Fig. 1). The third new signal in ^{13}C-NMR spectrum at chemical shift 64 ppm is proposed to be due to CH_2 of ethoxy group which is bonded to zirconium. ^{29}Si-NMR spectrum of catalyst 1 (Fig. 3) shows one extra signal compared to modified S1 at chemical shift δ -39 ppm due to the silane bearing the amine group. In the IR spectrum of catalyst 1 there were two new bands at wavenumbers 2802 and 2774 cm^{-1} which are assigned to CH stretching of CH_3N group. The two bands at different wavenumbers indicate that the dimethylamine group has been bonded to two different sites (Zr or Si).

According to the chemical analysis, IR, ^{13}C- and ^{29}Si-NMR results the following conclusions can be drawn. The zirconium is coordinated to one surface

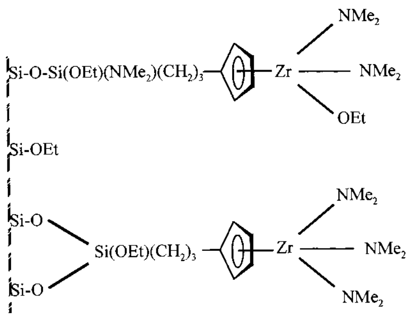

Fig. 1. The structure of the supported catalyst.

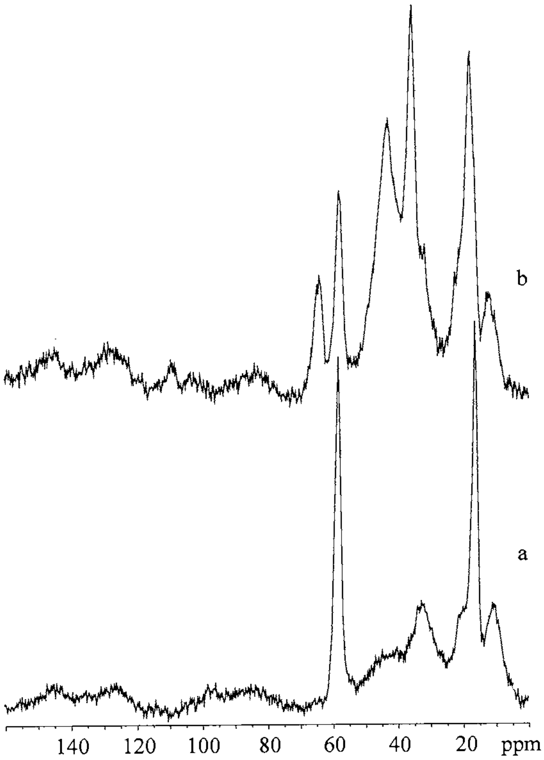

Fig. 2. ^{13}C-CPMAS-NMR spectra of (a) modified silica S1 and (b) catalyst 1.

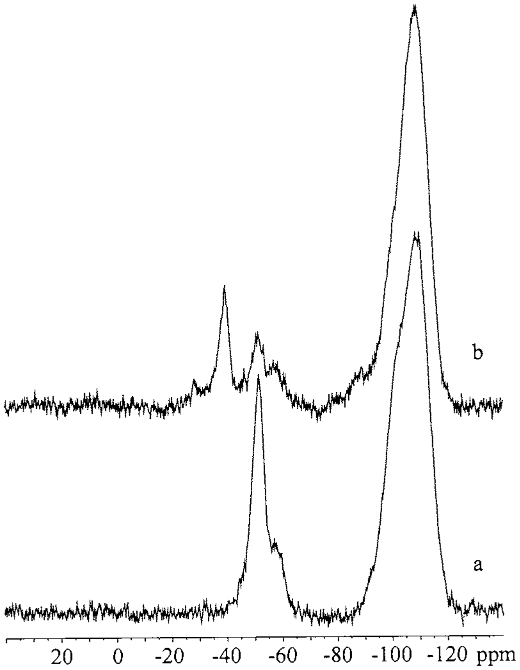

Fig. 3. ^{29}Si-CPMAS-NMR spectra of (a) modified silica S1 and (b) catalyst 1.

cyclopentadienyl group. Jordan with co-workers have reported [3d] that the equilibrium between mono- and bis-cyclopentadienyl complexes of $Me_2Si(Ind)_2Zr(NMe_2)_{2-3}$ strongly favors the mono-cyclopentadienyl complex which supports our findings. The exchange reaction between ethoxy and amine groups could occur and there are two to three amine and zero to one ethoxy groups coordinated to zirconium as depicted in Fig. 1.

To overcome the problem caused by reaction of ethoxy groups support S2 was first treated with methyllithium in order to alkylate the ethoxy groups and prevent the exchange reaction between the ethoxy and amide groups. The use of methyllithium caused besides the methylation of the ethoxy groups also the methylation of the silica surface and the surface cyclopentadienyl groups. The results from the methylation are described in detail elsewhere [7]. After the methylation there are four new signals in the ^{29}Si-NMR spectrum at δ 1.0, -0.7, -20 and -47 ppm. The resonances at δ -0.7, -20 and -47 ppm are due to a direct interaction of methyllithium with the silica surface. The resonance at δ 1 ppm is due to substitution of methyl for ethoxy group. The ^{13}C-NMR spectrum showed one new signal at a chemical shift of δ 1.8 ppm due to the methyl groups bound to silicon. The ethoxy group signals at δ 13 and 58 ppm had decreased in size indicating that ethoxy groups had been displaced by methyl. The surface cyclopentadienyl resonances had diminished clearly due to the methyllithium treatment which converts the cyclopentadienyl groups to anions. This was also visible in the IR spectrum (Fig. 4) where the reaction of support with methyllithium causes the disappearance of the weak band due to η^1-cyclopentadienyl band at 3044 cm^{-1}.

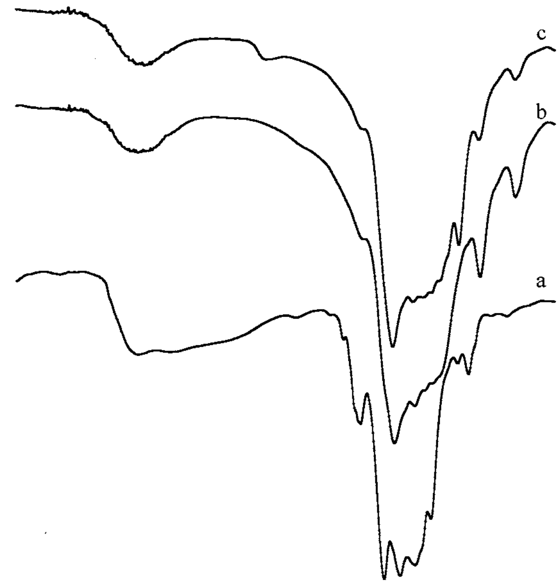

Fig. 4. FTIR spectra of (a) modified silica S2, (b) S2 treated with MeLi, and (c) catalyst 2.

Table 1
Results of ethylene polymerization [a] and the properties of the polymers

Catalyst	Amount of zr (mol)	Al/Zr	Yield (g)	A_g ($g\ g^{-1}$ Zr h)	Am ($kg\ mol^{-1}$ Zr h)	Tm (°C)	M_w ($g\ mol^{-1}$)	M_w/M_n
1. SiO_2–Cp/$Zr(NMe_2)_4$	2.0E−05	1300	1.9	1 100	100	137.2	207 000	1.9
2. SiO_2–Cp/MeLi/$Zr(NMe_2)_4$	5.4E−06	4100	4.6	9 400	860	133.5	192 000	1.9
3. $(Me_3SiCp)2Zr(NMe_2)_2$-	2.2E−06	1100	24	120 000 [b]	11 000 [b]	137.8	146 000	1.7
Cp_2ZrCl_2	2.2E−06	1000	40	200 000 [b]	18 000 [b]	–	–	–

[a] Polymerization conditions: temperature 80°C, pressure 2.5 bar, and time 30 min.

[b] Polymerization time 20 min.

The reaction of tetrakis(dimethylamino)zirconium with the methyllithium treated modified silica was made in a way similar to that of catalyst 1. The methyllithium treatment of S2 caused a decrease in the amount of zirconium on the surface. The zirconium contents of catalyst 2 was 1.58 w%, corresponding to the Zr loading of ca. 0.2 mmol g^{-1} or 0.3 atoms nm^{-2} which denotes Cp:Zr ratio of 2.0. The diminution of zirconium contents was caused by the lower number of Cp groups on the surface due to the different pre-treatment temperature of the silica. The exchange reaction between ethoxy and amide groups was at least partly prevented due to the displacement of the ethoxy by the methyl groups. The nitrogen contents of catalyst 2 was 0.45 w% which denotes N:Zr ratio of ca. 1.9 indicating that zirconium is co-ordinated to the two surface cyclopentadienyl groups and two dimethylamine groups have been eliminated. The ^{13}C-NMR spectrum of catalyst 2 shows only one extra signal at δ 37 ppm due to methyl group of amine which indicates that zirconium is bonded only in one way to the surface. In the ^{29}Si-NMR spectrum the signal at chemical shift δ -39 ppm caused by the dimethylamino group bound to the silicon is absent and there was one unidentified new signal at chemical shift δ -23 ppm compared to methyllithium treated support. In the IR spectrum there was only one NCH_3 band in the CH stretching region at wavenumber 2772 cm^{-1}. According to these findings the zirconium is co-ordinated to two surface cyclopentadienyl groups and it has two dimethylamine groups in its co-ordination sphere due to the prevention of the exchange reaction between ethoxy and amine groups. One reason for different co-ordination of zirconium in these two supported catalysts 1 and 2 could be that the zirconium bound ethoxy groups, which may act as 2–6 electron donors [8], can prevent the co-ordination of the second cyclopentadienyl group.

3.2. Preparation of the $(Me_3SiCp)_2Zr(NMe_2)_2$

The reaction of $Zr(NMe_2)_4$ with Me_3SiCp was used to prepare a model compound for the heterogeneous catalysts. The starting materials react easily with amine elimination in hexane when the mixture is slightly heated producing a yellow biscyclopentadienyl zirconium compound, $(Me_3SiCp)_2Zr(NMe_2)_2$, catalyst 3. The corresponding reaction between Me_3SiCp and $Ti(NMe_2)_4$ gave monocyclopentadienyl complex $(Me_3SiCp)Ti(NMe_2)_3$ instead of bis-substituted metallocene [7]. The different reactivity of the zirconium and titanium can be explained with steric reasons. The structure of catalyst 3 was confirmed by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra and elemental analysis. In the IR spectrum of the $(Me_3SiCp)_2Zr(NMe_2)_2$ two bands which are caused by η^1-cyclopentadienyl group of Me_3SiCp at wavenumbers 3091 and 3073 cm^{-1} had disappeared and two bands in a CH stretching region at wavenumbers 2812 and 2764 cm^{-1} due to dimethylamine group appeared.

3.3. Polymerization of ethylene

The activities of the catalysts (1–3) were tested in polymerization of ethylene in the presence of a co-catalyst MAO. The heterogeneous (catalysts 1 and 2) and homogeneous (catalyst 3 and Cp_2ZrCl_2) polymerizations were made in the same reactor and under the same unoptimized polymerization conditions. The results of polymerizations and polymerization conditions are summarized in Table 1. Zirconocene dichloride as a reference catalyst showed the highest activity of the tested catalysts. Homogeneous catalyst 3 was found to be significantly more active than heterogeneous catalysts 1 and 2 which corresponds to results presented for supported metallocenes in literature [4a]. The activities could have been higher if the metallocene amide complexes had been methylated before polymerization processes. [9] Heterogeneous bis-cyclopentadienyl complex, catalyst 2, was found to have higher activity than heterogeneous monocyclopentadienyl complex, catalyst 1. This parallels the results in literature where bis-cyclopentadienyl complex, Cp_2ZrCl_2, possessed higher activity for polymerization of ethylene than monocyclopentadienyl complex, $CpZrCl_3$ [5a,10].

The melting temperatures, the molecular weights and molecular weight distributions of polyethylenes are given in Table 1. The melting temperatures between 133.5 and 137.8°C are typical for linear high-density polyethylene. The polymers prepared with heterogeneous catalysts 1 and 2 have higher molecular weights than the polymer prepared with homogeneous catalyst 3. In recently reported studies the correlation between catalyst activity and molecular weight explains the difference in molecular weights. The higher the activity of the ethylene polymerization is, the lower the molecular weight of the polyethylene is [4a]. Monocyclopentadienyl complex, $CpZrCl_3$, produces higher molecular weight polyethylene than bis-cyclopentadienyl complex, Cp_2ZrCl_2 [5a, 10]. All systems produce polymer with narrow molecular weight distributions which is typical for polymers prepared with single-site catalysts. The IR spectrum of polymer prepared with catalyst 3 shows besides the three typical doublets of polyethylene also a very weak band at 1385 cm^{-1} which is assigned to bending of terminal methyl groups indicating minor branching in polymer. There are no evidence of branching in the IR spectra of polymer made with heterogeneous catalysts 1 or 2.

4. Conclusions

Heterogeneous ethylene polymerization catalysts were prepared by immobilizing the tetrakis(dimethylamino)zirconium on the chemically modified silica surface. Bis- and monocyclopentadienyl zirconium amide complexes were formed in the reaction of zirconium compound with surface cyclopentadienyl groups via the amine elimination reaction with and without the help of methyllithium, respectively. The methyllithium is needed to alkylate ethoxy groups of the silane coupling agent, $Cp(CH_2)_3Si(OEt)_3$. A homogeneous model compound was prepared by convenient reaction between trimethylsilylcyclopentadienyl and tetrakis(dimethylamino)zirconium. All the prepared homo- and heterogeneous catalysts are active in the polymerization of ethylene in the presence of a cocatalyst MAO and they produce linear high-density polyethylene. Further studies concerning modified cyclopentadienyl surfaces with transition metals and their use in catalytic processes are in progress in our laboratory and will be reported in the future.

Acknowledgements

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