

Synthesis of supported titanocene amide complex and its use as a catalyst in ethylene polymerization

Sari Timonen^a, Tuula T. Pakkanen^{a,*}, Eero I. Iiskola^b

^a Department of Chemistry, University of Joensuu, Yliopistokatu 7, P.O. Box 111, FIN-80101 Joensuu, Finland

^b VTT Chemical Technology, P.O. Box 1401, FIN-02044 VTT, Finland

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Abstract

Heterogeneous ethylene polymerization catalysts were prepared by supporting tetrakis(dimethylamino)titanium, $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$, on chemically modified silica surface. The modification of silica was made using a silane coupling agent, $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ and atomic layer chemical vapor deposition (ALCVD). Titanium amide was also immobilized straight on the silica and on a methyl lithium-treated modified silica. The aim of methyl lithium treatment was to alkylate the unreacted ethoxy groups of the silane coupling agent on the silica. Methyl lithium methylates, besides ethoxy groups, also silica surface and surface cyclopentadienyl groups. A model compound for these heterogeneous catalysts was prepared using a reaction of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ with trimethylsilylcyclopentadienyl yielding a monocyclopentadienyl titanium compound, $\text{Me}_3\text{SiCpTi}[\text{N}(\text{CH}_3)_2]_3$. The preliminary results of ethylene polymerization using the prepared heterogeneous and homogeneous titanocene amide complexes and the effect of amount of MAO are presented. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of the catalytic properties of metallocenes in olefin polymerization [1–3], a lot of effort has been paid to develop new catalysts for practical use. The metallocene compounds have been studied intensively due to their high influence on microstructure and molecular weight of the (co)polymer. The metallocene dichloro complexes, like the widely

studied $\text{EtInd}_2\text{ZrCl}_2$ [4–9], are difficult to prepare and yields are generally moderately low. Therefore, recently, it has been reported that the transition metal amide complexes of the type $\text{M}(\text{NR}_2)_4$ are excellent precursors for the synthesis of *ansa*-metallocenes and bridged half-sandwich complexes [10–15].

In practice, the modern industrial polymerization processes require 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 [16–21]. The silica-supported catalysts are

* Corresponding author. Tel. +358-13-251-3340; Fax: +358-13-251-3344; E-mail: tuula.pakkanen@joensuu.fi

generally less active in polymerization of ethylene than their homogeneous counterparts, but in some cases the activity can be improved by modifying the silica support [22–26].

In this paper we report the preparation of a supported metallocene amide that is an active catalyst in ethylene polymerization. The catalyst is prepared by a convenient amine elimination reaction between cyclopentadienyl modified silica surface and tetrakis(dimethylamino)titanium. The support was moreover pretreated with methylolithium in order to study the effect of unreacted ethoxy groups of the coupling agent on the structure of the catalyst. The metallocene amide compound $(\text{CH}_3)_3\text{SiCpTi}[\text{N}(\text{CH}_3)_2]_3$ was also studied as a homogeneous model for heterogeneous systems and the ethylene polymerization activities of both systems will be presented.

2. Experimental

2.1. General procedures

All reactions were carried out under nitrogen atmosphere using the glovebox and Schlenk techniques. Silica (EP 10, Crosfield) with a surface area of $320 \text{ m}^2/\text{g}$, pore volume of $1.8 \text{ cm}^3/\text{g}$, and mean particle size of $100 \mu\text{m}$ was used as a support. The surface modification of silica was carried out by using the saturated gas–solid reactions of a silane coupling agent, $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, and a partially dehydroxylated silica as described previously [22]. Solvents, diethyl ether, hexane and toluene, were dried and deoxygenated by distillation over sodium-benzophenone ketyl. $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ (Inorgtech.) and $\text{CpSi}(\text{CH}_3)_3$ (97%, Fluka) were used in synthesis without further purification. Methylaluminoxane (10% and 30% MAO in toluene) was purchased from Witco. 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 the catalysts

IR spectra were recorded by a Nicolet Impact 400D spectrometer equipped with a diffuse reflectance accessory. 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 5 ms contact time, 5 s delay and 15 000 transients. ^{13}C CPMAS NMR spectra were obtained at 100.6 MHz with 3 ms contact time, 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. Titanium analyses were carried out with Perkin–Elmer 4100 atomic absorption spectrometer.

2.3. Polymer analysis

The melting temperatures of the polyethylenes were measured with a Mettler Toledo Star DSC 821 system of powdered samples. The samples were heated first at a heating rate of $20^\circ\text{C}/\text{min}$, cooled and melted again at the heating rate of $10^\circ\text{C}/\text{min}$, and the second heating curve was analyzed. Molecular weights and molecular-weight distributions of the polyethylene samples were determined using a Waters 150 C instrument equipped with three Waters Styragel HT3, HT4, and HT6 columns. The solvent, 1,2,4-trichlorobenzene, was applied at a flow rate of $1.0 \text{ ml}/\text{min}$. The basic calibration was made by using polystyrene standards with a narrow molecular-weight distribution and the universal calibration with a linear low-density polyethylene.

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 atomic layer chemical vapor deposition (AL-CVD) reactor. Preheated silica was reacted with $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}(\text{CH}_2)_3\text{Cp}$ at 280°C under nitrogen flow for 2 h. Carbon analysis found for materials: Si, 6.7; S2, 5.0%. ^{13}C CPMAS NMR: δ 11 (CH_2), 16 (OCH_2CH_3), 21 (CH_2), 33 (CH_2), 45 (Cp), 58 (OCH_2CH_3), 127 (Cp) and 145 (Cp) ppm. ^{29}Si CPMAS NMR: δ -110 (silica), -57 ($\text{RCH}_2(\text{OCH}_2\text{CH}_3)_2\text{Si}(\text{OSiO}_3)_2$) and -52 ($\text{RCH}_2(\text{OCH}_2\text{CH}_3)_2\text{Si}(\text{OSiO}_3)$) ppm.

2.5. Reaction of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ with the support (S1)

The hexane solution of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ (0.16 ml, 0.7 mmol) was added dropwise to the hexane suspension of the modified silica (1.5 g, 0.7 mmol Cp). 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, 1.94; Ti, 3.28; C, 8.83 w%. ^{13}C CPMAS NMR: δ 12 (CH_2), 17 (OCH_2CH_3), 21 (CH_2), 32 (CH_2), 39 ($\text{SiN}(\text{CH}_3)_2$), 42 ($\text{TiN}(\text{CH}_3)_2$), 48 ($\text{TiN}(\text{CH}_3)_2$), 58 (OCH_2CH_3), 127 (Cp) and 146 (Cp) ppm. ^{29}Si CPMAS NMR: δ -108 (silica), -59 ($\text{RCH}_2(\text{OCH}_2\text{CH}_3)_2\text{Si}(\text{OSiO}_3)_2$), -52 ($\text{RCH}_2(\text{OCH}_2\text{CH}_3)_2\text{Si}(\text{OSiO}_3)$) and -40 ($\text{RCH}_2(\text{OCH}_2\text{CH}_3)(\text{N}(\text{CH}_3)_2)\text{Si}(\text{OSiO}_3)$) ppm.

2.6. Reaction of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ with neat silica

The hexane solution of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ (0.12 ml, 0.5 mmol) was added dropwise to the hexane suspension of the silica (1.1 g). The mixture was refluxed for 5 h and stirred at room temperature overnight. The solid part was separated and washed three times with hexane and dried under vacuum at 40°C. Elemental analysis found for material: N, 1.84; Ti, 2.7; C, 3.88 w%. ^{13}C CPMAS NMR: δ -0.3 (SiCH_3), 39 ($\text{SiN}(\text{CH}_3)_2$), 42 ($\text{TiN}(\text{CH}_3)_2$), and 48 ($\text{TiN}(\text{CH}_3)_2$) ppm. ^{29}Si CPMAS NMR: δ -108

(silica), -19 ($\text{Si-O-TiN}(\text{CH}_3)_2$), and -22 ($\text{Si-O-TiN}(\text{CH}_3)_2$) ppm.

2.7. Reaction of methyllithium with the silica

Into the suspension of silica (1.0 g) in diethyl ether was added excess of methyllithium (5 ml, 1.6 M in diethyl ether). The mixture was stirred at room temperature overnight. The solid part was separated and washed three times with diethyl ether and dried under vacuum. ^{13}C CPMAS NMR: δ -0.2 ppm. ^{29}Si CPMAS NMR: δ -108 (OSiO_3), -93 (SiOLi), -80 ($\text{Si}(\text{OLi})_2$), -48 (SiCH_3), -20 ($\text{Si}(\text{CH}_3)_2$), -1 ($\text{Si}(\text{CH}_3)_3$) and 8 ($\text{Si}(\text{CH}_3)_4$) ppm.

2.8. Reaction of methyllithium with the support (S2)

Into the suspension of modified silica (2.0 g, 1 mmol Cp) in diethyl ether was added excess of methyllithium (10 ml, 1.6 M in diethyl ether). The mixture was stirred at room temperature overnight. The solid part was separated and washed three times with diethyl ether and dried under vacuum. Carbon analysis found for material: 7.4%. ^{13}C CPMAS NMR: δ 2 (SiCH_3), 13 ($(\text{CH}_3)\text{Cp}$), 17 (OCH_2CH_3), 22 (CH_2), 34 (CH_2), 45 (Cp), 58 (OCH_2CH_3), 65 (unassigned), 102 (unassigned), 126 (Cp) and 144 (Cp) ppm. ^{29}Si CPMAS NMR: δ -108 (OSiO_3), -95 (SiOLi), -82 ($\text{Si}(\text{OLi})_2$), -47 (SiCH_3), -20 ($\text{Si}(\text{CH}_3)_2$), -1 ($\text{Si}(\text{CH}_3)_3$), 1 ($(\text{RCH}_2\text{Si}(\text{CH}_3)_2(\text{OSiO}_3))$) and 6 ($\text{Si}(\text{CH}_3)_4$) ppm.

2.9. Reaction of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ with the methyllithium-treated support (S2)

Into the suspension of methyllithium-treated modified silica (0.7 g, 0.3 mmol) in hexane was

added excess of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ (0.2 ml, 0.8 mmol) in hexane. The mixture was refluxed 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, 0.2; Ti, 0.8; C, 7.33 wt%. ^{13}C CPMAS NMR: δ 2 (SiCH_3), 18 (OCH_2CH_3), 22 (CH_2), 37 ($\text{TiN}(\text{CH}_3)_2$), 58 (OCH_2CH_3) ppm. ^{29}Si CPMAS NMR: δ -109 (OSiO_3), -90 (SiOLi), -80 ($\text{Si}(\text{OLi})_2$), -48 (SiCH_3), -21 ($\text{Si}(\text{CH}_3)_2$), -2 ($\text{Si}(\text{CH}_3)_3$), 1 ($(\text{RCH}_2\text{Si}(\text{CH}_3)_2(\text{OSiO}_3))$) and 7 ($\text{Si}(\text{CH}_3)_4$) ppm.

2.10. $\text{Me}_3\text{SiCpTi}[\text{N}(\text{CH}_3)_2]_3$

A hexane solution of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ (1.4 ml, 6.7 mmol) was added dropwise to a hexane solution of $(\text{CH}_3)_3\text{SiCp}$ (2 ml, 12.1 mmol). The mixture was stirred at room temperature for 6 h. The solvent was evaporated yielding a dark yellow liquid. Elemental analysis calculated for $\text{C}_{14}\text{H}_{31}\text{N}_3\text{SiTi}$: C, 52.98; H, 9.84; N, 13.24. Found: C, 52.73; H, 9.94; N, 13.71%. ^1H NMR (toluene- d_8): δ 0.26 (s, $\text{Si}(\text{CH}_3)_3$), 3.08 (s, $[\text{N}(\text{CH}_3)_2]$), 6.10 (m, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8): δ 0.41 ($\text{Si}(\text{CH}_3)_3$), 50.2 ($\text{N}(\text{CH}_3)_2$), 113.1 (Cp), 118.3 (Cp), 119.7 (Cp). ^{29}Si NMR (toluene- d_8): δ -7.38 ppm.

2.11. Polymerization of ethylene

Ethylene was polymerized in a 0.5 dm^3 stainless-steel Büchi autoclave. The catalyst suspended in toluene, MAO as a cocatalyst and toluene as a reaction media were placed into the reactor batchwise under nitrogen flow. The amount of MAO used in the polymerization corresponded to the Al/Ti 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 polymerization was terminated by the addition of acidic ethanol into the reactor. 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 catalyst

The surface modification of silica was carried out by using a saturated gas–solid reaction of a silane coupling agent $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ with a partially dehydroxylated silica in an AL-CVD reactor. In contrast to traditional silica modification methods reported in literature [25] the modification of silica with ALCVD technique is facile and the possible effects of the solvent have been eliminated. The silica was preheated at 600° (S1) or 820°C (S2) and after the modification reaction at 280°C the carbon contents of supports were 6.7 wt.% corresponding to 0.9 Cp/nm^2 and 5 wt.% corresponding to 0.6 Cp/nm^2 , respectively. The presence of cyclopentadienyl alkoxy silane 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, $-(\text{CH}_2)_3-$ [22].

Tetrakis(dimethylamino)titanium was attached to the cyclopentadienyl functionalized silica surface of S1 with a liquid phase reaction in hexane. The reaction between metal amide and cyclopentadienyl proceeds with an amine elimination and does not require the use of alkyl lithium reagent and therefore one step in catalyst preparation and the inconvenience due to the coordination of THF are thus eliminated. After the $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ treatment the titanium content of the supported catalyst (catalyst 1) was 3.3 wt.%, corresponding to the Ti loading of ca. 0.7 mmol/g or 1.3 Ti atoms/nm^2 of support hence there are more than one Ti atoms for each cyclopentadienyl group (0.9 Cp/nm^2) on the surface. The nitrogen content of the catalyst was 1.9 wt.% which denotes a N/Ti ratio of 2. In the IR spectrum of catalyst 1 two new bands at wavenumbers 2815 and 2769 cm^{-1} assigned to CH stretching of the CH_3N

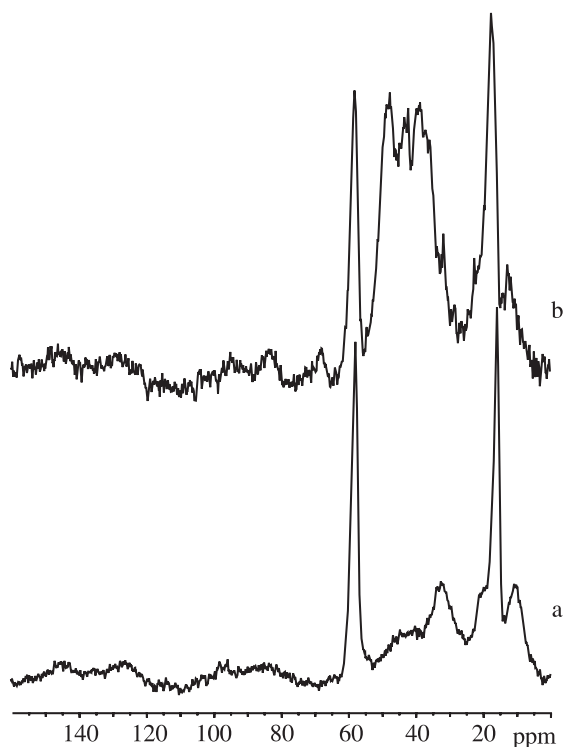
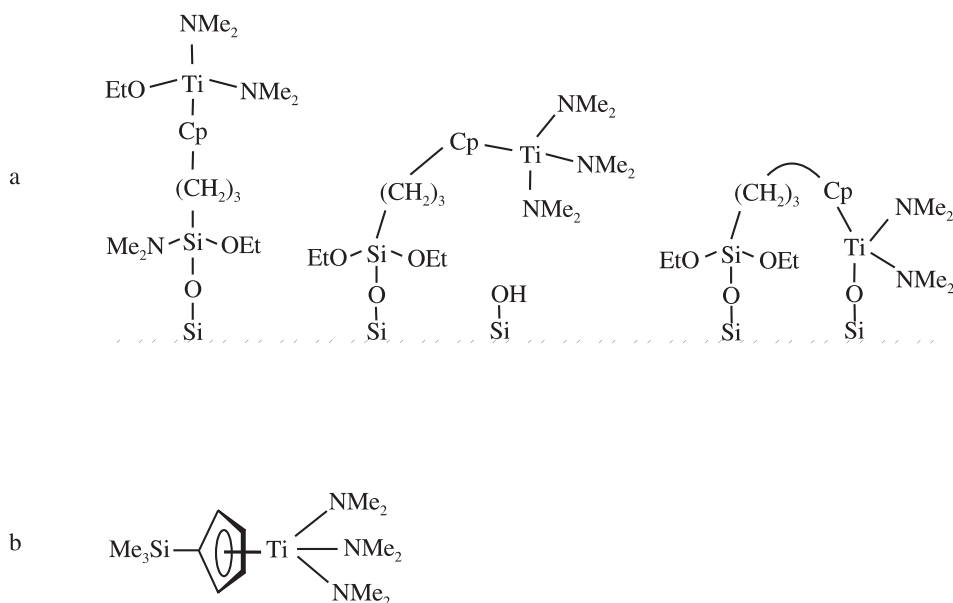


Fig. 1. ^{13}C CPMAS NMR spectra of (a) modified silica S1 and (b) catalyst 1.

group were observed due to amine groups in two different coordination spheres. The ^{29}Si NMR spectrum of catalyst 1 shows one extra signal compared to modified support 1 at chemical shift $\delta -40$ ppm due to silicon of the silane coupling agent containing dimethylamine groups. The exchange reaction between dimethylamine of titanium and ethoxy groups of the silane coupling agent occurs and titanium has either three dimethylamine groups or two dimethylamine and one ethoxy group in its coordination sphere. In the ^{13}C NMR spectrum (Fig. 1) the resonances due to surface cyclopentadienyl have diminished and the three new resonances due to methyl groups of amide occurred at chemical shifts $\delta 39$, 42 and 48 ppm. The signal at $\delta 39$ ppm is assigned to be dimethylamine that is bound to silicon of the silane coupling agent [27] via exchange reaction between amine and ethoxy groups. The signals at $\delta 42$ and 48 ppm are due to the amine groups of titanium.

A reaction between titanium amide and neat silica revealed that the titanium reacts easily



Scheme 1. The proposed structure of (a) supported catalyst 1 and (b) homogeneous catalyst 3.

with surface hydroxyl or surface siloxane groups. After the reaction titanium and nitrogen contents on silica were 2.7 and 1.7 wt.% which denotes a N/Ti ratio of 2.2. According to the elemental analysis and IR, ^{13}C and ^{29}Si NMR it is reasonable to assume that the titanium in catalyst 1 has been coordinated to surface cyclopentadienyl group as well as to the surface itself. In another possible coordination mode the titanium is coordinated to one surface cyclopentadienyl group as well as to a surface hydroxyl group yielding a ring structure on the surface as depicted in Scheme 1. These coordination modes were enabled by the hydroxyl groups which had remained on the surface after the modification.

To overcome the exchange reaction between amine and ethoxy groups support 2 was first treated with methyllithium in order to alkylate the ethoxy groups. In addition support 2 has been calcinated at 820°C in order to decrease the hydroxyl content on surface and to prevent the titanium reaction with the surface. In order to find out the effect of CH_3Li treatment on the unmodified silica neat silica was first treated with methyllithium. The methyllithium treatment of silica causes a methylation of the silica surface [28] (Eqs. (1)–(3)) which can be seen from the ^{13}C , ^{29}Si NMR and IR spectra of the methyllithium-treated silica. After the methylation there are seven resonances in the ^{29}Si NMR spectrum at chemical shift δ 6, -1 , -20 , -47 , -82 , -95 and -108 ppm (Fig. 2). The high field resonance at -108 ppm of the silica surface assigned to be silicon with no methyl groups in its surroundings has changed its shape which is caused by replacement of hydrogen of the hydroxyl group by lithium atom and/or by rearrangement of the surface due to the methylation. The lower field resonances at δ -47 , -20 , -1 and 8 ppm are caused by different levels of methylation of the silica surface, that is, one, two, three and four methyl groups bonded to the surface silicon, respectively. Tetramethylsilane is probably blocked in the pores of the silica. The ^{13}C NMR spectrum shows one sharp and strong signal at chemical

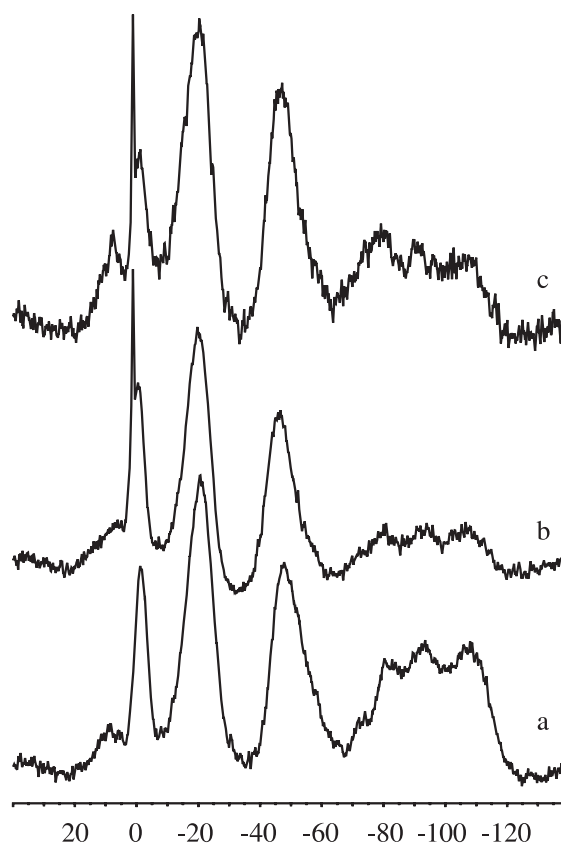
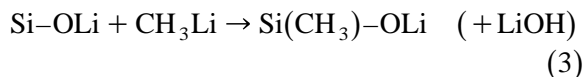
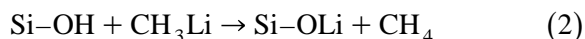
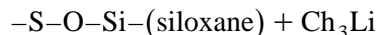


Fig. 2. ^{29}Si CPMAS NMR spectra of (a) CH_3Li -treated silica, (b) CH_3Li -treated modified silica S2, and (c) catalyst 2.

shift δ -0.2 due to the methyl group bonded to the silicon atom of the surface.



The methyllithium treatment of modified support 2 causes one new resonance at δ 1 ppm in the ^{29}Si NMR spectrum compared to the ^{29}Si NMR spectrum of CH_3Li -treated silica due to

substitution of methyl for ethoxy group (Eq. (4)). The ^{13}C NMR spectrum (Fig. 3) showed one broad signal at δ 1.8 ppm due to the methyl groups bonded to silicon. A sharp signal at chemical shift δ 13 ppm due to the methylation of the cyclopentadienyl ring has appeared. The intensities of the ethoxy signals at δ 13 and 58 ppm have decreased indicating that some of ethoxy groups are displaced by methyl. The surface cyclopentadienyl resonances had diminished clearly due to the methyllithium treatment which indicates that surface cyclopentadienyl groups are converted to anions in the reaction with methyllithium. That is also visible in the IR spectrum where the reaction of support S2 with methyllithium causes the disappearance of the weak band due to η^1 -cyclopentadienyl group at 3044 cm^{-1} . This observation indicates that electronic nature of the surface cyclopentadienyl

has changed as a result of the reaction with the lithium. In the IR spectrum there are two strong bands at wavenumbers 2898 and 2952 cm^{-1} which are assigned to be symmetric and asymmetric CH stretching mode of the NCH_3 group. There are also two unidentified signals in the ^{13}C NMR spectrum of the CH_3Li -treated support 2 at chemical shifts δ 65 and 102 ppm. The resonance at 102 ppm is visible also in the spectrum of support 2 and could be caused by either an impurity on the surface or a difference in the surface structure caused by the higher pretreatment temperature of the silica.

The reaction of tetrakis(dimethylamino)-titanium with methyllithium-treated modified silica was made in a similar way as the reaction of titanium compound with modified silica without methyllithium pretreatment. The methyllithium treatment of support S2 caused a decrease in the amount of bound titanium on the surface. The titanium contents of catalyst 2 was 0.8 wt.%, corresponding to the Ti loading of ca. 0.2 mmol/g or 0.3 atoms/nm^2 . The diminution of titanium contents was due to the higher pretreatment temperature of the silica which leads to a lower content of hydroxyl groups and therefore to a lower Cp surface density. The nitrogen contents of catalyst 2 was 0.2 wt.% which denotes a N/Ti ratio of ca. 1. One reason for the small N/Ti ratio could be that the nitrogen content is too low to give reliable results in the chemical analysis. The ^{13}C NMR spectrum (Fig. 3) shows only one extra signal at 37 ppm due to methyl group of amide which indicates that titanium is bonded in only one way to the surface. In the ^{29}Si NMR spectrum of catalyst 2 (Fig. 2) there was no change compared to methyllithium-treated support which verifies that the exchange reaction between the ethoxy and amine groups has been prevented. In the IR spectrum there was only one new band in the CH stretching region at wavenumber 2772 cm^{-1} due to the CH stretching of CH_3N group. According to the chemical analysis and IR and NMR spectra the titanium amide in catalyst 2 is bonded to one or two surface cyclopentadienyl groups.

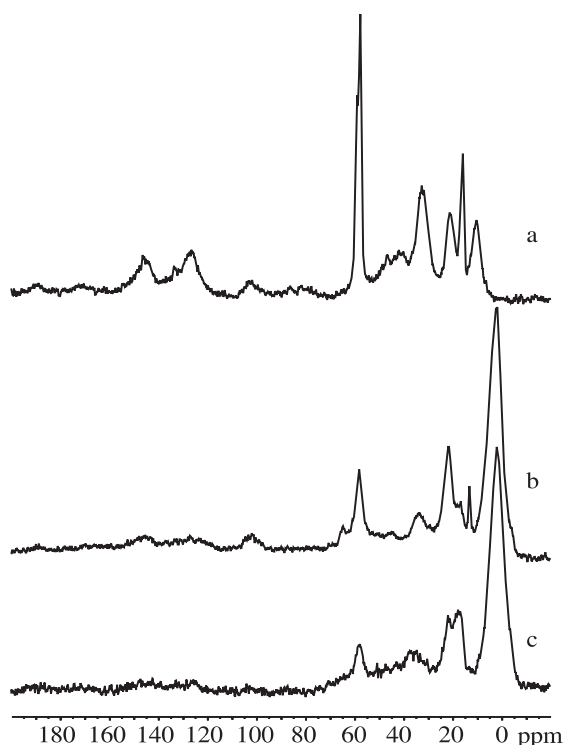


Fig. 3. ^{13}C CPMAS NMR spectra of (a) modified silica S2, (b) CH_3Li -treated modified silica S2, and (c) catalyst 2.

3.2. Preparation of the $(\text{CH}_3)_3\text{SiCpTi}[\text{N}(\text{CH}_3)_2]_3$

The reaction of $(\text{CH}_3)_3\text{SiCp}$ and $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ was studied as a model reaction in the preparation of the homogeneous polymerization catalyst. The starting materials react by amine elimination in hexane at room temperature within a few hours producing a monocyclopentadienyl titanium compound $(\text{CH}_3)_3\text{SiCpTi}[\text{N}(\text{CH}_3)_2]_3$, (catalyst 3). We found that $(\text{CH}_3)_3\text{SiCp}$ eliminates only one amine ligand from $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ even with twofold amount of ligand and with heating the system as shown earlier by Chandra and Lappert [15]. The corresponding reaction between Me_3SiCp and $\text{Zr}[\text{N}(\text{CH}_3)_2]_4$ produces doubly substituted complex $(\text{Me}_3\text{SiCp})_2\text{Zr}[\text{N}(\text{CH}_3)_2]_2$ instead of monocyclopentadienyl complex [29]. The different reactivity of the zirconium and titanium has been explained with steric reasons [15]. The structure of catalyst 3 presented in Scheme 1 was confirmed by ^1H , ^{13}C , and ^{29}Si NMR spectra and elemental analysis. In the IR spectrum of the $(\text{CH}_3)_3\text{SiCpTi}[\text{N}(\text{CH}_3)_2]_3$ two bands which are caused by the η^1 -cyclopentadienyl group of $(\text{CH}_3)_3\text{SiCp}$ at wavenumbers 3096 and 3077 cm^{-1} had disappeared and two bands in a CH stretching region at wavenumbers 2812 and 2764 cm^{-1} due to dimethylamino group had appeared.

3.3. Polymerization of ethylene

The activities of the catalysts were tested in the polymerization of ethylene in the presence

of a cocatalyst, MAO. The heterogeneous (catalysts 1 and 2) and homogeneous (catalyst 3) polymerizations were carried out in a Büchi polymerization reactor under the same unoptimized polymerization conditions (toluene as a reaction media, ethylene pressure of 2.5 bar, temperature of 80°C and reaction time of 30 min). The results of polymerization and polymerization conditions are summarized in Table 1. In general, using the Al/Ti ratio of 1000 the activities of the supported catalysts 1 and 2 are in the same order of magnitude as that of the homogeneous catalyst 3. The Al/Ti ratio has a large effect on the polymerization activities of catalysts 1–3. A large amount of MAO is needed to methylate the catalysts before polymerization [30]. Increasing the Al/Ti ratio from 1000 to 4000 increases the activity of homogeneous catalyst 1 and heterogeneous catalyst 2 by 40- and 30-fold, respectively. Thus Al/Ti ratio has a bigger effect upon the homogeneous system than upon the heterogeneous system.

The melting temperatures of polymers are given in Table 1. They are between 131.4° and 139.2°C which are typical for linear high-density polyethylene. The molecular weight of one of the polymers was measured. The molecular weight of the polyethylene prepared with the homogeneous polymerization where the Al/Ti ratio was 4000 was 241 000 and the molecular-weight distribution was 2.2 which is typical for polymers prepared with single-site metallocene catalysts. The IR spectra of polymers show, besides the three typical doublets of polyethylene, also a weak band at 1385 cm^{-1} which

Table 1
Results of ethylene polymerization^a

| Catalyst | Support | <i>n</i> of Ti (mol) | Al/Ti | Yield (g) | <i>A_m</i> (kg/mol Ti h) | <i>T_m</i> (°C) |
|----------|---------|----------------------|-------|-----------|---------------------------------------|---------------------------|
| 1 | S1 | 2.5E – 05 | 1000 | 0.73 | 30 | 139.2 |
| 2 | S2 | 4.5E – 06 | 1000 | 0.08 | 19 | – ^b |
| 2 | S2 | 5.2E – 06 | 4000 | 2.84 | 550 | 131.4 |
| 3 | – | 6.3E – 06 | 1000 | 0.28 | 44 | 139.0 |
| 3 | – | 6.3E – 06 | 4000 | 11.2 | 1800 | 138.1 |

^aPolymerization conditions: temperature 80°C , pressure 2.5 bar, and time 30 min.

^bNot determined.

is assigned to bending of terminal methyl groups and indicates a slight branching in the polymer.

4. Conclusions

Heterogeneous ethylene polymerization catalysts containing cyclopentadienyl dimethylaminotitanium surface groups were prepared by immobilizing the tetrakis(dimethylamino)titanium on the Cp-functionalized silica surface. The reaction of titanium compound with surface cyclopentadienyl proceeds easily via an amine elimination reaction yielding monocyclopentadienyl titanium compound with dimethylamine and ethoxy groups coordinated to titanium. The ethoxy group of the titanium is a result of the exchange reaction between ethoxy of the silane coupling agent and dimethylamine groups. The methylolithium was used to alkylate unreacted ethoxy groups of the silane coupling agent, $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$. The use of methylolithium could be avoided by using monoethoxysilane, e.g., $\text{Cp}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OCH}_2\text{CH}_3$, as surface modifier. The methylolithium as a very reactive reagent reacts, besides the ethoxy groups, also with the surface cyclopentadienyl groups and directly with the silica yielding methylated surface. A homogeneous model compound was prepared by a convenient reaction between trimethylsilylcyclopentadienyl and tetrakis(dimethylamino)titanium. Supporting the titanium amide compound on the modified silica does not reduce the polymerization activity, since the activities of the heterogeneous catalysts are comparable to that of the homogeneous analog. The activity strongly depends on the Al/Ti ratio and the ratio seems to have a bigger effect upon the homogeneous than upon the heterogeneous polymerization system. 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.

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