Cyclopentadienyl Surface as a Support for Zirconium Polyethylene Catalysts

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ABSTRACT: A novel ethylene polymerization catalyst is prepared by supporting $CpZrCl_3$ on chemically modified silica. The surface modification of silica was carried out by utilizing the saturated gas−solid reactions of a silane coupling agent, $Cp(CH_2)_3Si(OCH_2CH_3)_3$, and a partially dehydroxylated silica. Immobilization of $CpZrCl_3$ onto the cyclopentadienyl surface formed on the silica was done using liquid-phase reactions. The stepwise-prepared materials were characterized by ^{13}C and ^{29}Si solid state NMR and FT-IR spectroscopy. This supported catalyst system has a high activity and can be used to produce polyethylene with a narrow molecular weight distribution in the presence of methylaluminoxane. The immobilization of $CpZrCl_3$ on the cyclopentadienyl surface of SiO_2 more than doubled the polymerization activity of $CpZrCl_3$. However, the direct heterogenization of $CpZrCl_3$ onto an unmodified, partially dehydroxylated silica produced a catalyst with a very low activity. The effect of surface modification reactions and structure of the support on the catalyst performance is presented and discussed.

Introduction

Since the discovery of homogeneous metallocene compounds and the methylaluminoxane cocatalyst that combines high activity[1] with stereoregularity[2,3] in the polymerization of α-olefins, much effort has been paid to modifying the metallocene catalysts for practical use. 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 polymerization activity of the silica-supported catalysts can be improved by modifying the silica with Cl_2SiMe_2.[5a]

One approach for the immobilization of metal complexes on SiO_2 supports involves the use of silane coupling agents.[5b−e] The cyclopentadienyls have been used as ligands for anchoring metallocene complexes on the silica support utilizing silanes containing cyclopentadienyl groups directly bonded to the silicon atom.[5f,g] However, the polymerization activity of these catalysts per gram of solid support has been very low.

In this paper we report a stepwise preparation of a supported zirconium polymerization catalyst, where the silica is modified in a new way. The surface modification of silica was carried out by utilizing the saturated gas−solid reactions[6,7] of a silane coupling agent, $Cp(CH_2)_3Si(OCH_2CH_3)_3$, where the cyclopentadienyl group is separated from the silicon atom with a hydrocarbon spacer, $-(CH_2)_3-$. The zirconium compound, $CpZrCl_3$, was immobilized on the modified silica with liquid-phase reactions. The stepwise preparation of the supported zirconium metallocene polymerization catalysts was followed by solid state ^{13}C and ^{29}Si NMR as well as by FT-IR spectroscopy. The performance of this procatalyst was tested in ethylene slurry polymerization in the presence of methylaluminoxane (MAO).

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Experimental Section

All reactions were carried out under nitrogen using the standard inert atmosphere techniques.

Reagents. Silica (EP 10, Crosfield Ltd.) with a surface area of 320 m^2/g, pore volume of 1.8 cm^3/g, and mean particle size of 100 μm was used as a support. THF and diethyl ether were deoxygenated and dried by distillation under nitrogen over sodium−benzophenone ketyl. $(EtO)_3Si(CH_2)_3Cp$ (ABCR GmbH & Co.) and $CpZrCl_3$ (Strem Chemicals) were used without further purification. All products were stored in a Vacuum Atmospheres glovebox under nitrogen.

Methylaluminoxane (10% MAO in toluene) was purchased from Witco GmbH. The *n*-heptane (Merck, purum) used as the reaction medium for polymerizations was purified by circulating the liquid through three columns containing molecular sieves, activated Cu, and Al_2O_3. Ethylene (AGA, grade 3.5) was passed through a purification train containing molecular sieves, activated Cu, and Al_2O_3 just before feeding to the reactor. Toluene (Riedel-de-Haën AG, grade RG) used for the catalyst suspension was dried with molecular sieves before use and stored under nitrogen.

Modification of Silica. SiO_2 was preheated at 200 °C (carrier B) or 600 °C (all other carriers) for 16 h in air. The saturated gas−solid reactions were carried out in a commercial F-120 ALE (Atomic Layer Epitaxy) reactor manufactured by Microchemistry Ltd. Preheated silica (5−9 g) was brought to the reaction temperature at a pressure of 6−10 kPa under a flow of nitrogen. Then, 6 mL of $(EtO)_3Si(CH_2)_3Cp$ was vaporized at 200 °C, and the vapor was led into a reaction chamber kept at a selected temperature for 2 h through a solid silica bed, supported on a sinter.[7] The reaction temperature was 200 °C for samples B and C and 250 °C for sample D. After this, the reactor was flushed with a nitrogen stream at the reaction temperature for an additional hour. The samples were cooled in a nitrogen flow and transferred into a glovebox.

Preparation of the Supported Catalyst. Into a suspension of modified silica (C, 2.5 g) in THF was added a solution of butyllithium (1.5 mL, 3.75 mmol) in hexane. The mixture was kept under vigorous stirring at room temperature overnight. The solid part was separated and washed three times with THF. A THF solution of $CpZrCl_3$ (0.37 g, 1.4 mmol) was

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added dropwise into a suspension of the obtained silica in THF. The mixture was stirred at room temperature overnight. The final solid (catalyst **4**) was separated and washed with THF and diethyl ether and then dried under vacuum at 45 °C overnight. Catalysts **3**, **5**, and **6** were prepared with the same method.

Three different reference catalysts were prepared. Catalysts **1** and **2** were prepared by starting from unmodified silica (A). For reference catalyst **1** the unmodified silica was treated with a THF solution of $CpZrCl_3$. Reference catalyst **2** was prepared by treating the unmodified silica with butyllithium before it was treated with a THF solution of $CpZrCl_3$. Reference catalyst **7** was prepared from modified silica (D) by treating it directly with a THF solution of $CpZrCl_3$.

Polymerization Procedure. Ethylene homopolymerizations were performed in *n*-heptane in a 1.0 dm^3 stainless steel autoclave. *n*-Heptane (660 cm^3) was introduced into the evacuated and N_2-purged reactor. Methylaluminoxane (MAO), used as cocatalyst, was added batchwise under N_2 flow. The amount of MAO used in the polymerization corresponded to the Al/Zr molar ratio of 1500 or 2000. The weighed amount of heterogeneous catalyst was suspended in 30 mL of toluene and transferred into the reactor under N_2 pressure. For some polymerizations MAO and the catalyst were allowed to prereact in the reactor at the polymerization temperature for 5 or 10 min. The feeding of ethylene was then begun, and the ethylene pressure in the reactor was regulated to 2.5 bar. The consumption of ethylene was followed with a mass flow controller. The polymerization temperature was set to 80 °C, and the polymerization time to 30 min. After the polymerization, the reactor was degassed. The polymerization product was stirred with a mixture of ethanol and a small amount of concentrated hydrochloric acid and filtered. Finally, the polymer was washed with ethanol with magnetic stirring, filtered, and dried.

Characterization of the Supported Catalysts. Chemical Analysis. Zirconium was determined by X-ray fluorescence (XRF) and carbon with a LECO-CHN600 analyzer. Chloride was determined by potentiometric titration with $AgNO_3$ after dissolving the weighed sample into a 3.5 M sulfuric acid solution.

SEM/EDS Analysis. An epoxy resin-coated silica particle was cut in half and analyzed by a scanning electron microscope equipped with an energy dispersive spectrometer (SEM/EDS). The method is described in more detail elsewhere.[7a]

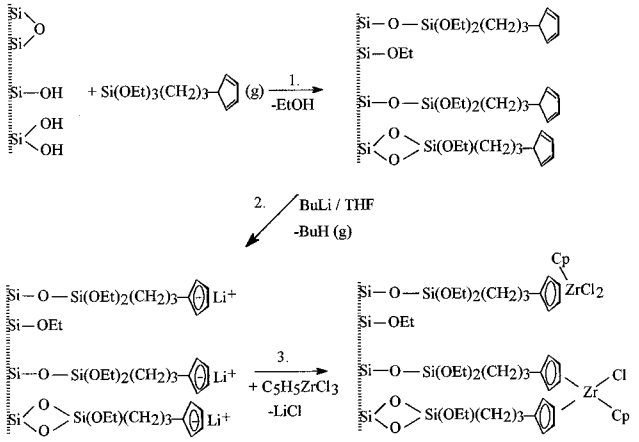
FTIR Measurements. IR spectra were measured by an FTIR spectrometer (Nicolet Magna-IR Spectrometer 750) equipped with a diffuse reflectance accessory and connected airtightly to a glovebox. The samples were measured under a nitrogen atmosphere as loosely packed powders with a 2 cm^{-1} spectral resolution. The accumulation time was 1 min, corresponding to 50 scans.

NMR Measurements. 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 experiments were recorded at 79.5 MHz with a 5 ms contact time, 5 s delay, and 15 000 or 17 000 transients. ^{13}C CPMAS NMR spectra were obtained at 100.6 MHz with a 3 ms contact time, 4 s delay, and 20 000 transients. All experiments were carried out using a spinning speed of 4.5 kHz.

Polymer Analysis. Molecular weights and molecular weight distributions of the polyethylene samples were determined using a Waters 150 ALC/GPC instrument equipped with three Waters Styragel columns (exclusion limits for polystyrene 10^3, 10^4, and 10^6 Å). The solvent, 1,2,4-trichlorobenzene, was applied at a flow rate of 1.0 cm^3/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.

The melting temperatures of the polyethylenes were measured with a Polymer Laboratories DSC system. The analyzed samples were in a powder form. The samples were heated twice at the heating rate of 10 °C/min, cooled between the meltings, and the second heating curve was analyzed.

Scheme 1. Modification of Silica with $Cp(CH_2)_3Si(OEt)_3$ and Preparation of Supported Catalyst.



Results and Discussion

Modification of the Silica Support. The surface modification of silica was carried out using a reaction of the saturated $Cp(CH_2)_3Si(OCH_2CH_3)_3$ gas with the solid silica surface at elevated temperatures. Cermák et al.[11] have found that the dimerization of a monosubstituted cyclopentadienyl silane coupling agent is a serious obstacle in the surface functionalization of oxide supports when the reactions are performed in the liquid state. To avoid this problem, we heated up the neat $Cp(CH_2)_3Si(OCH_2CH_3)_3$ in a vacuum and evaporated the monomer formed from the $[Cp(CH_2)_3Si(OCH_2CH_3)_3]_2$ dimer. At elevated temperatures (>200 °C), all of the reactive groups of silica will interact with the monomeric silane gas until the surface is saturated.

The relative amounts of the different reactive sites on the silica surface can be controlled by the degree of calcination of the silica. After heat treatment above 450 °C, silica contains mainly isolated (single and to a smaller extent geminal) hydroxyl groups.[7] The number of OH groups in silica after calcination at 600 °C (for 16 h) is approximately 1.8−1.9/nm^2, of which about 1.5−1.6/nm^2 are isolated silanol groups, the rest being internal silanol groups unable to interact. Furthermore, the dehydroxylated silica contains hydrophobic siloxane bridges that have been found to be even more reactive than isolated or geminal hydroxyl groups.[8,9] The reaction mechanism of the strained siloxanes of silica with alkoxysilanes has recently been confirmed by Blumel[10] using solid state NMR spectroscopy. On the whole, the heat-treated silica contains three types of reactive surface groups, as depicted in Scheme 1.

Pretreatment of the silica was done with calcination either at 200 or 600 °C (carriers B and A, C−D, respectively, in Table 1). The heat treatment at 200 °C (16 h) removes all the physisorbed water present in silica. The infrared spectrum of this dehydrated silica exhibits a broad hydroxyl band at 3200−3700 cm^{-1}, which is characteristic of the hydrogen-bonded hydroxyl groups, as well as a strong band at 3745 cm^{-1}, which can be assigned to isolated OH groups.[7] The silica powder dehydrated at 600 °C (16 h, carrier A) shows a simple infrared spectrum (Figure 1a or 3a), with only one sharp band at 3745 cm^{-1} due to the isolated OH groups.

The surface modification of the dehydrated silica with $Cp(CH_2)_3Si(OCH_2CH_3)_3$ was carried out at two different temperatures (200 or 250 °C). The reaction with silane causes the disappearance of the sharp band of silica at

Table 1. Modification of Silica and Preparation and Analysis of the Supported $CpZrCl_3$ Catalysts

catalyst	carrier	T_{calc} (°C)	T_{modif} (°C)	$m_{carrier}$ (g)	amt of BuLi (mmol)	amt of $CpZrCl_3$ (mmol)	[Zr] (w %)	[Cl] (w %)	Cl/Zr mole ratio
1	A	600		2.5		1.4	0.9	0.7	2.00
2	A	600		2.2	2.5	1.2	2.2	1.47	1.75
3	B	200	200	6.0	7.5	3.2	3.4	1.4	1.06
4	C	600	200	2.5	3.75	1.4	3.1	1.1	0.92
5	D	600	250	2.5	3.75	1.3	3.0	1.1	0.94
6	D	600	250	5.1	7.5	2.7	3.0	1.1	0.94
7	D	600	250	2.0		1.1	0.3	< 0.1	

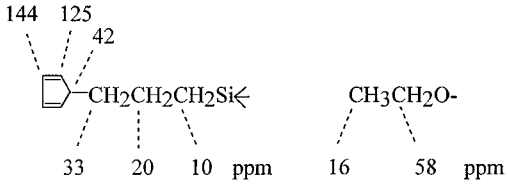
Table 2. ^{29}Si and ^{13}C Chemical Shifts (δ) of the Carriers

carrier	$RCH_2(OC_2H_5)_nSi(OSiO_3)_{3-n}$	$HOSi(OSiO_3)_3$	$Si(OSiO_3)_4$	OCH_2CH_3	$(CH_2)_3$	Cp
A		−101.12	−110.13			
B	−46.40, −51.13, −58.36	−101.93	−111.58	16.03, 58.06	10.67, 20.52, 33.24	42.01, 125.41, 144.88
C	−45.78, −50.53, −56.63	−100.21	−108.00	15.91, 57.80	10.35, 20.59, 32.73	41.99, 125.41, 146.57
D	−52.43, −58.78	−101.21	−109.51	17.95, 59.58	12.02, 22.05, 34.69	43.84, 127.44, 148.00
$(EtO)_3Si(CH_2)_3Cp$	−44.89					

Table 3. ^{29}Si and ^{13}C Chemical Shifts (δ) of the Catalysts

catalyst	SiBu	$RCH_2(OC_2H_5)_nSi(OSiO_3)_{3-n}$	$HOSi(OSiO_3)_3$	$Si(OSiO_3)_4$	OCH_2CH_3	$(CH_2)_3$	Cp	CpZr
2			−101.00	−110.04				115.34
3	13.53	−51.55, −58.72	−101.91	−111.27	17.31, 57.83	11.59, 21.73, 34.60	40.75, 125.63, 144.51	114.33
C/BuLi	3.32, 14.24	−51.65, −58.91	−100.11	−109.25	16.20, 57.53	11.61, 34.46	41.51, 125.89, 146.49	
4	3.70, 14.17	−51.62, −58.55	−100.02	−108.59	15.93, 58.02	11.90, 34.21	41.27, 125.40, 144.20	114.35
5	2.54, 13.52	−52.46, −58.96	−101.21	−109.38	17.11, 58.40	11.60, 33.28	41.47, 126.48, 146.02	113.81
6	3.16, 13.7	−52.23, −58.22		−107.84	18.35, 58.58	11.73, 34.79	125.09, 146.27	114.36
7		−52.66, −58.22		−109.55	18.12, 59.75	12.48, 23.18, 35.09	43.25, 127.94, 147.90	
Cp_2ZrCl_2[a]								115.7
$CpZrCl_3$[a]								118.2

[a] In toluene-d_8.



3745 cm^{-1} and the appearance of a new broad band at 3100−3600 cm^{-1}. The latter band can be assigned to the hydroxyl groups of silica perturbed by hydrogen-bonding interactions with oxygen atoms of the ethoxy groups of silane (see Figure 1b or 2a).[13] The disappearance of the isolated OH band at 3745 cm^{-1} could lead to a straightforward assumption that all the OH groups have reacted and that the silica surface has been saturated with the silane coupling agent. However, we have found[12] that at the lower reaction temperatures, all the reactive surface groups are not able to react with silane gas because of steric reasons or strong hydrogen bonding present in the dehydrated silica.

The modification of the silica surface was also confirmed with ^{13}C CP/MAS NMR spectroscopy. The ^{13}C resonances of the surface-bound silane were observed at 15 and 58 ppm due to the CH_3 and CH_2 carbons of ethoxy groups, respectively, and at 11, 20, and 33 ppm due to the CH_2 carbons of $\equiv SiCH_2CH_2CH_2Cp$ as well as at 42, 125, and 144 ppm due to the Cp ring carbons (see Table 2 and Figure 5a).

The presence of cyclopentadienyl alkoxysilane on the silica surface was observed using ^{29}Si CP/MAS NMR spectroscopy. The modified silica materials showed major resonances at −102 and −111 ppm due to the $(\equiv SiO)_3SiOH$ and $(\equiv SiO)_4Si$ groups of silica, respectively. In the case of the $(\equiv SiO)_3SiOH$ groups, ^{29}Si CP/MAS NMR is not able to distinguish silicon atoms located on the surface or inside the bulk silica matrix.[7] Resonances at −51 and −58 ppm are due to the silicon atoms of the bound $\equiv SiCH_2CH_2CH_2Cp$ moiety (see Table 2 and Figure 4). These two low-field resonances have been assigned to the silicon atoms of the silane bound to the silica surface with one siloxane and two siloxane bonds, respectively. According to the ^{29}Si spectrum of carrier C in Figure 4, $Cp(CH_2)_3Si(OCH_2CH_3)_3$ binds to the silica surface mostly with monodentate and less with bidentate linkages. No signal at −66 ppm corresponding to the formation of three siloxane linkages was observed.[14] The obvious reason for this

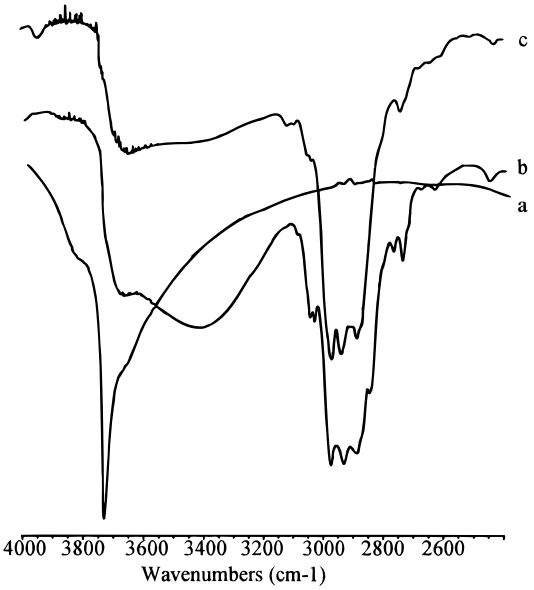


Figure 1. FTIR spectra of (a) neat SiO_2 (A), (b) carrier D, and (c) D treated with BuLi and $CpZrCl_3$ (catalyst **5**).

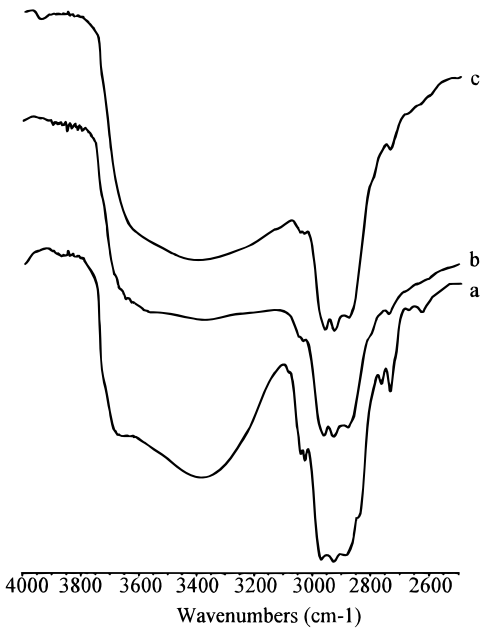


Figure 2. FTIR spectra of (a) carrier C, (b) C treated with BuLi, and (c) C treated with BuLi and $CpZrCl_3$ (catalyst **4**).

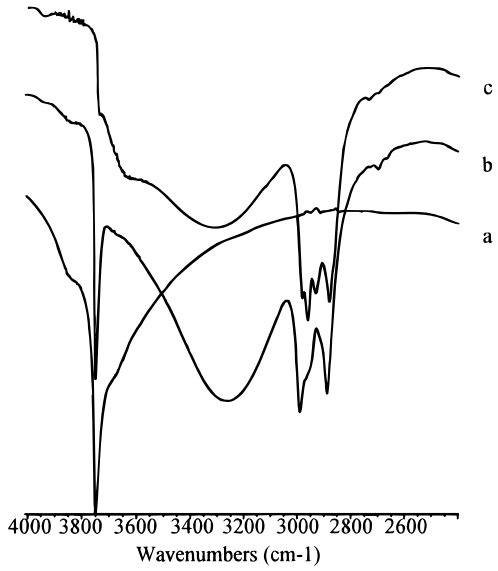


Figure 3. FTIR spectra of (a) neat SiO_2 (A), (b) A treated with $CpZrCl_3$ (catalyst 1), and (c) A treated with BuLi and $CpZrCl_3$ (catalyst **2**).

is the low OH surface density due to the high pretreatment temperature of silica. In the ^{29}Si NMR spectra of the materials modified at 200 °C (carrier C, Figure 4a), a resonance at −46 ppm was observed. The chemical shift corresponds to that of the neat $Cp(CH_2)_3Si(OCH_2CH_3)_3$. Due to the low vapor pressure of $Cp(CH_2)_3Si(OCH_2CH_3)_3$ at the reaction temperature of 200 °C, condensation of cyclopentadienyl alkoxysilane can probably occur in silica pores. The −46 ppm resonance was not observed in the ^{29}Si NMR spectra of the modified silica, in which the modification reaction had been carried out at 250 °C.

Based on the IR as well as the ^{13}C and ^{29}Si NMR results, the saturated gas−solid reaction between $Cp(CH_2)_3Si(OCH_2CH_3)_3$ and the silica yields a modified silica with a cyclopentadienyl surface. When the reaction conditions have been optimized, the gas−solid reaction produces modified materials with a uniform quality. The carbon contents of 6.4−6.9 w % measured

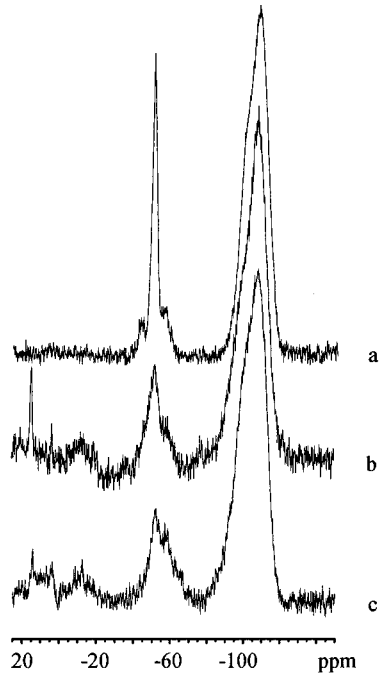


Figure 4. ^{29}Si CPMAS NMR spectra of (a) carrier C, (b) C treated with BuLi, and (c) C treated with BuLi and $CpZrCl_3$ (catalyst **4**).

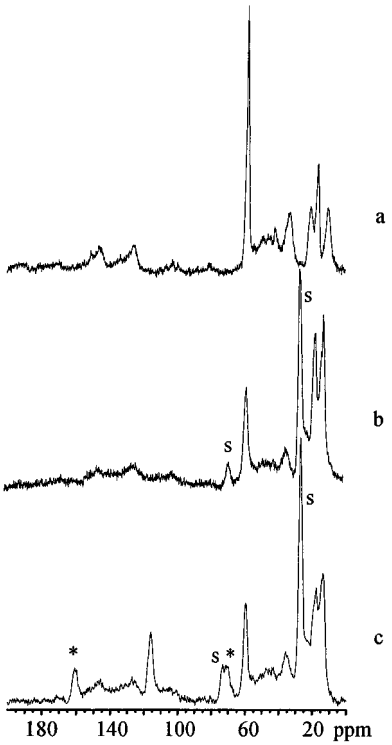


Figure 5. ^{13}C CPMAS NMR spectra of (a) carrier C, (b) C treated with BuLi, and (c) C treated with BuLi and $CpZrCl_3$ (catalyst **4**). s denotes a solvent. * denotes a spinning side band.

for the carriers of type D are very similar. This carbon content range corresponds approximately to the Cp surface density of 0.8−0.9 Cp rings/nm^2.

Preparation of the Supported Catalysts. Since the inorganic and organometallic chemistry of surfaces is very versatile, one must know the wide variety of reactions involved to avoid the pitfalls, especially in scaling up a commercially attractive catalyst. As we can notice later in the text, every reaction step in the preparation of a supported metallocene catalyst has an

enormous effect on the elemental composition and/or performance of the catalyst.

Cyclopentadienylzirconium trichloride was attached to the modified silica surface in two steps described in the scheme. The modified silica was first treated with an excess of *n*-butyllithium to convert the cyclopentadienyl groups to anions capable of further reaction with a transition metal compound. An excess of $CpZrCl_3$ was used in the preparation of the supported catalyst when compared to the estimated number of cyclopentadienyl groups on the surface. The zirconium and chloride contents of the thus obtained catalysts are presented in Table 1. Depending on the surface modification of the silica, the zirconium contents of the catalysts prepared (**1**−**7**) varied from 0.3% to 3.4 w %, corresponding to the Zr loadings of ca. 0.03−0.4 mmol/g or 0.07−0.8 atoms/nm^2 of support.

Based on the chemical analysis, the immobilization of $CpZrCl_3$ directly on the unmodified silica changes the Cl/Zr ratio of the zirconium compound from 3 to 2 (catalyst **1**). This result indicates that $CpZrCl_3$ is bound on the silica solely in a monodentate form via a replacement of surface OH groups and the elimination of HCl. The reaction does not take place to any great extent. The Zr content of catalyst **1** is only 0.9 w %, and the IR spectrum (Figure 3b) shows a strong band at 3745 cm^{-1} due to isolated Si−OH groups. A butyllithium pretreatment of the unmodified silica reduces the Cl/Zr ratio to some extent and more than doubles the amount of Zr on the support (catalyst **2**). The OH band at 3745 cm^{-1} in the IR spectrum (Figure 3c) has also disappeared, indicating the complete reaction of the isolated OH groups of silica. On the other hand, the reaction of $CpZrCl_3$ with the cyclopentadienyl surface of SiO_2 changes the chemical composition of the zirconocene compound, since the Cl/Zr ratio decreases from the value of 3 in the starting compound to the value of 1 (in catalysts **4**−**6**). The final chemical composition of the zirconium species can be explained by a reaction (eqs 1 and 2) of excess butyllithium with the ethoxy groups of the supported silane and/or silica surface producing lithium ethoxide.[15]

$$\text{silica surface}-O-Si(OEt)_2(CH_2)_3Cp + BuLi \rightarrow \text{silica surface}-O-Si(Bu)(OEt)(CH_2)_3\,Cp + LiOEt \quad (1a)$$

$$\text{silica surface}-O-Si(Bu)(OEt)(CH_2)_3Cp + BuLi \rightarrow \text{silica surface}-O-Si(Bu)_2(CH_2)_3Cp + LiOEt \quad (1b)$$

$$\text{silica surface}-OEt + BuLi \rightarrow \text{silica surface}-Bu + LiOEt \quad (2)$$

LiOEt reacts further with the cyclopentadienylzirconium trichloride or the surface-anchored Zr species giving $CpZrCl_2(OEt)$ or silica surface$-O-SiR_2(CH_2)_3$-Cp(Cp)ZrCl(OEt), respectively (eq 3).

$$LiOEt + CpZrCl_3 \rightarrow CpZrCl_2(OEt) + LiCl \quad (3)$$

Another possible explanation for the low Cl/Zr ratio is that cyclopentadienylzirconium trichloride binds to two surface cyclopentadienyl groups instead of one, and a tris(cyclopentadienyl)zirconium chloride complex is formed.[16] Our preliminary molecular modeling results indicate that Cp groups on the modified surface at the surface density corresponding to the actual experimental conditions are close enough to facilitate the coordination of zirconium to two Cp rings of the cyclopentadienyl surface.

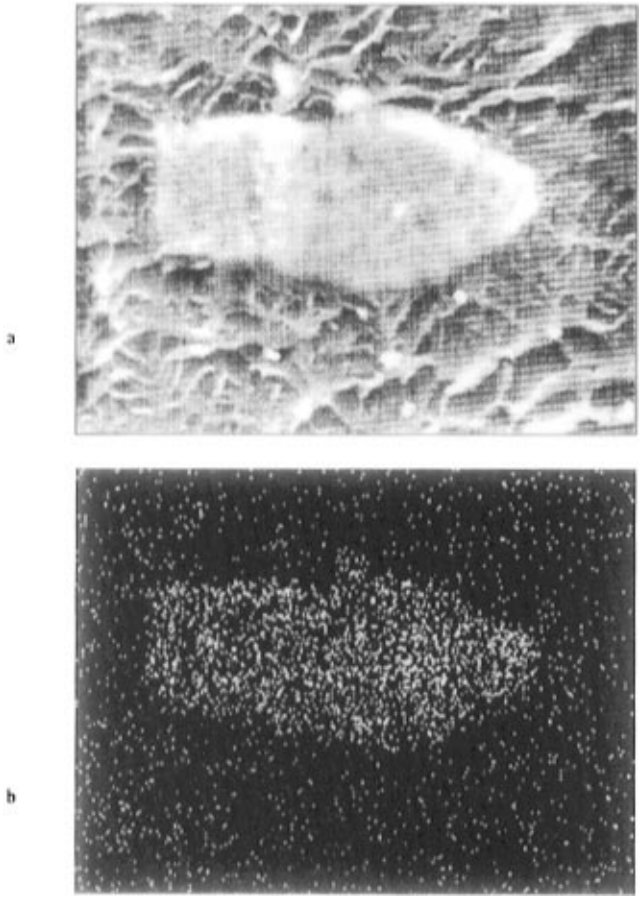


Figure 6. Distribution of zirconium inside a silica particle of catalyst **5** measured by SEM/EDS. Photographs: (a) original particle; (b) Zr distribution.

Characterization of the supported $CpZrCl_3$ materials with ^{29}Si NMR spectroscopy indicates that the above liquid phase reactions performed on the modified silica surface change the monodentate structure of $O-Si(OEt)_2(CH_2)_3Cp$, as is evidenced by the changes in the shapes of the signals at −52 and −58 ppm (Figure 4). Moreover, one or two low-field sharp resonances at 13.5 and 3 ppm can be seen and are assigned to the silicon nuclei attached to one or two butyl groups (formed in reactions 1), respectively. The broad low-field signal at −10 ppm probably originates from the surface silicon nuclei possessing butyl groups (reaction 2). Observation of the ^{13}C NMR resonances (δ ca. 26 and 13 ppm) of these new butyl groups is obscured by the overlaps of the CH_2 resonances of the $(CH_2)_3$ moiety of $O-Si(OEt)_2(CH_2)_3Cp$ (δ 11 ppm) and the THF solvent residue (δ 25 ppm) (Figure 5).

The structural characterization of $CpZrCl_3$ on the modified silica is based on the IR and ^{13}C NMR results. In the ^{13}C NMR spectrum of catalyst **4** (Figure 5c) a new, relatively sharp low-field signal appears at 115 ppm, originating from a Cp group bonded to zirconium. In the IR spectrum of catalyst **4** (Figure 2c) there is a weak band at 3946 cm^{-1}, which is typical of a η^5-Cp group. These results indicate that $CpZrCl_3$ binds to the modified silica with the Cp ligand intact. Yet, they do not reveal the attachment mode of $CpZrCl_3$, since the same signals are also observed in the IR and ^{13}C NMR spectra of the catalysts in which $CpZrCl_3$ is supported directly on silica or on the BuLi-pretreated silica. However, the IR spectra (Figures 1 and 2) show that

Table 4. Polymerizations of Ethylene with Homogeneous and Heterogeneous Cp Catalysts and Properties of the Polymers[a]

catalyst	amt of catalyst (mol)	yield (g)	activity g of PE/(g of cat.·h)]	activity kg of PE/(mol of Zr·h)]	M_w	M_n	M_w/Mn	T_m (°C)
Cp_2ZrCl_2[b,c]	3.42×10^{-6}	30.7		8980	98 000	36 000	2.72	138.9
$CpZrCl_3$[b]	4.19×10^{-6}	2.5		1200	233 000	85 000	2.73	140.6
1	8.43×10^{-6}	1.1	26	260	221 000	89 000	2.47	141.7
2	4.22×10^{-6}	1.4	160	660	135 000	51 000	2.63	135.8
3	2.85×10^{-6}	1.8	460	1300	197 000	70 000	2.80	138.9
4	21.1×10^{-6}	11	360	1000	103 000	47 000	2.22	138
5	4.21×10^{-6}	5.1	800	2400	119 000	48 000	2.48	137.7
6	8.3×10^{-6}	12.1	964	2930	109 000	43 000	2.5	136.0
7	3.3×10^{-6}	0.85	17	520	195 000	81 000	2.4	136.4

[a] Polymerization conditions: temperature 80 °C, pressure 2.5 bar, and time 30 min. [b] Homogeneous polymerization. [c] Polymerization time 1 h.

the intensities of the characteristic bands of the η^1-cyclopentadienyl groups of the modified silica at 3030 and 3045 cm^{-1} have decreased after the reaction with BuLi and $CpZrCl_3$. This observation indicates that the electronic nature of the surface-bound Cp has changed as a result of the above surface reactions and supports the formation of surface-anchored Cp′$CpZrCl_2$ or Cp′$_2$-$CpZrCl$ species, where Cp′ indicates a cyclopentadienyl group of the modified surface (see the scheme). The transformation of the surface-bonded Cp group cannot be easily followed with ^{13}C NMR spectroscopy, since the resonances due to the silica-bound Cp are very broad. Most of the $CpZrCl_3$ species on the modified silica is bonded to the Cp groups of the silane coupling reagent on the basis of the very low Zr content of catalyst **7**, which has been prepared by a direct reaction of $CpZrCl_3$ with the modified silica without the BuLi pretreatment.

On the basis of the chemical analysis as well as on IR and NMR data, the parallel catalyst syntheses (e.g., catalysts **5** and **6**) are highly reproducible. The spatial distributions of zirconium and chlorine in the porous catalyst particle determined with SEM/EDS also indicate the high quality of the catalysts. The cross-section cut from a particle of catalyst **5** showed uniform macroscopic distributions of Zr (Figure 6) and Cl throughout the silica particle.

Polymerization of Ethylene. The activities of the supported $CpZrCl_3$ catalysts were tested in the polymerization of ethylene in the presence of a cocatalyst MAO (Al/Zr = 1500 or 2000). The results are presented in Table 4. For comparison, the activities of Cp_2ZrCl_2 and $CpZrCl_3$ as homogeneous catalysts were studied using the same polymerization system. The activity of the homogeneous Cp_2ZrCl_2 catalyst is found to be the highest (8980 kg of PE/(mol of Zr·h)), 7-fold higher than that of the homogeneous $CpZrCl_3$ (1200 kg of PE/(mol of Zr·h)). The best of the modified silica-supported $CpZrCl_3$ catalysts (catalyst **6**) gives the relatively high ethylene polymerization activity of 2930 kg of PE/(mol of Zr·h), which is more than twice that of the corresponding homogeneous $CpZrCl_3$ catalyst. This result clearly indicates the activation effect of the cyclopentadienyl surface of silica. Those catalysts, in which $CpZrCl_3$ is supported directly on the unmodified silica (catalyst **1**) or the BuLi-pretreated silica (catalyst **2**), showed very low activities, compared with that of the homogeneous $CpZrCl_3$ catalyst. A similar low activity was also observed for catalyst **7**, in which $CpZrCl_3$ is supported on the modified silica without a linkage to the cyclopentadienyl groups of the silane coupling agent. These polymerization results support the view that the anchoring of $CpZrCl_3$ to the modified silica occurs with direct bonds from zirconium to one or two Cp groups of the cyclopentadienyl surface.

Parallel catalysts **5** and **6** give comparable activities, indicating that the catalyst system is highly reproducible. The prereaction between the catalyst and cocatalyst before the charging of ethylene was found to have no significant effect on the polymerization activity.

Polymer Analysis. The molecular weights, molecular weight distributions, and melting temperatures of the polymers are given in Table 4. The polyethylene prepared with the homogeneous $CpZrCl_3$ catalyst has the highest molecular weight, whereas the molecular weight of the polyethylene prepared with the homogeneous Cp_2ZrCl_2 is the lowest. Molecular weights of the polyethylenes prepared with supported $CpZrCl_3$ catalysts are between the two former. The trend seems to be the higher the activity of the polymerization the lower the molecular weight of the polyethylene product. The molecular weight distributions of the polymers are narrow (around 2.5), which is typical for polymers prepared with metallocene catalysts. Melting temperatures from 135.8 to 141.7 °C were measured. These values are typical for linear HD polyethylene. The results from the polymer analysis indicate that these supported cyclopentadienylzirconium catalysts possess the single-site characteristics of the metallocene catalyst.

Conclusions

According to our knowledge, this is the first time that a homogeneous transition metal catalyst used in the polymerization of α-olefins has been activated by a cyclopentadienyl surface. The fact that the activity of the polymerization catalyst is more than doubled as compared with that of the corresponding homogeneous form is direct evidence of the surface activation effect without any loss of characteristics of the polymer produced. Besides polymerization parameters, the supported metallocene catalyst performance is decisively dependent on the preparation method used. The goal was to emphasize the importance of surface science in the heterogenization of metallocene catalysts. As we have shown, the catalyst activity level can be increased at least 10-fold in the polymerization of ethylene by choosing the proper surface structure for the heterogenization of $CpZrCl_3$. The surface structure varied from a deactivating surface (partially dehydroxylated silica) to an activating cyclopentadienyl surface. In the case of the cyclopentadienyl surface, the reactions of BuLi with the surface may have an impact on the catalyst performance. This could possibly be avoided using monoethoxysilanes (e.g., $Cp(CH_2)_3SiMe_2OEt$)[17] as surface modifiers. Further studies concerning modified cyclopentadienyl surfaces with transition metals and their use in catalytic applications are in progress in our laboratories and will be reported in the future.

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References and Notes

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(12) The interaction of surface hydroxyl groups of silica with alkoxysilanes is sensitive to the temperature used in saturated gas−solid reactions and heavily dependent on the properties of a reagent used. In other words the optimum reaction temperature, in which all the hydroxy groups have reacted, is very different for mono-, di-, or trialkoxysilanes, being highest for monoalkoxysilanes and lowest for trialkoxysilanes. For steric reasons all the hydroxy groups are not able to react with a gaseous silane monomer. This can be seen in the IR spectra where the broad absorbance is characteristic of hydrogen-bonding interactions between isolated surface silanol groups and oxygen atoms in chemisorbed $Cp(CH_2)_3Si(OEt)_3$ molecules. This broad infrared band is characteristic of the gas−solid reactions carried out at low reaction temperatures between silica and alkoxysilanes (Iiskola, E., unpublished results).
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