Chem. Mater. **2004,** *16,* 5713−5720

Preparation, Characterization, and Activity of Silica Supported Metallocene Catalysts

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Received May 17, 2001. Revised Manuscript Received September 17, 2004

Silica supported metallocene catalysts were prepared for ethylene polymerization by immobilizing bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) onto both calcined silica, and silica treated with γ-aminopropyltrimethoxysilane or γ-mercaptopropyltrimethoxy-silane. Bis(cyclopentadienyl)zirconium chloride hydride (Cp_2ZrClH) was also immobilized onto both calcined silica and vinyltrimethoxysilane treated silica. The catalysts were characterized by using direct current plasma atomic emission spectroscopy (DCP-AES), diffuse reflectance infrared spectroscopy (DRIFT), and X-ray photoelecton spectroscopy (XPS). It was found that both Cp_2ZrCl_2 and Cp_2ZrClH were adsorbed on both calcined silica and silane treated silica, respectively. When γ-aminopropyltrimethoxysilane (APTMS) was used as the spacer molecule, some of the amine became protonated upon adsorption of Cp_2ZrCl_2. Initial catalytic tests showed that all of the complexes were catalytically active (methylaluminoxane as a cocatalyst), with the Cp_2ZrClH supported complexes giving the highest activities, but still lower than the homogeneous catalyst, Cp_2ZrCl_2. The supported complexes produced polymer with higher molecular weight than the homogeneous catalyst. These observations, together with presented spectral evidence, support the view that the catalyst remained adsorbed in the presence of MAO.

Introduction

Single-site polyolefin catalysts, i.e., metallocenes with M = Zr, Hf, or Ti derivatives, combined with methylaluminoxane (MAO) as a cocatalyst have been the subject of intense research.[1−7] These systems efficiently catalyze α-olefin polymerization and the ligands at the transition metal center provide the possibility to tailor polymer properties such as molecular weight, molecular weight distribution, and stereoregularity.[8,9] High activities and good polymer properties have been obtained using homogeneous catalysts, but the supported catalysts are required for use in industry, e.g., in gas-phase and slurry polymerization processes.

Several research groups have prepared supported metallocene complexes by first activating the support (silica) with either ordinary alkylaluminas or MAO followed by addition of metallocene.[6,10−13] Collins et al.[11] have prepared supported *ansa*- metallocenes (M = Zr) which catalyze the formation of stereospecific polypropylene with a narrow molecular weight distribution. In a slightly different approach Soga et al.[14] have modified the silica gel with Me_2SiCl_2 before addition of the metallocene, then polymerized ethylene using trialkylaluminum cocatalysts. Highly isospecific catalysts for propene polymerization have also been prepared, by first immobilizing the metallocene ligand on silica and then adding zirconium compounds.[15] Supported zirconocene dichloride (Cp_2ZrCl_2, Cp = cyclopentadiene)/MAO catalysts had a decreased activity for ethylene polymerization as compared with the homogeneous system, polymer molecular weights increased, and the weight distribution remained narrow.[13] Recently, Atiqullah et al.[16] used X-ray photoelectron spectroscopy (XPS) to characterize silica supported $Et(Ind)_2ZrCl_2$ complexes.

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10.1021/cm0111229 CCC: $27.50

They concluded that cationic complexes were formed which could help explain why the catalytic activity of the supported complexes is generally lower. To increase the catalytic activity of supported systems it appears that pretreatment of the support is necessary.

In addition to the use of the cocatalyst as a modifier of the electronic activity at the surface sites[17] the support has been modified to enhance the activity of the catalyst. Alternatively, the silica support has been treated with a cross-linking agent (ethylene glycol, glycerol, and bisphenol A) to increase both the amount of zirconium adsorbed and the polymerization activity.[18] Moreover, to enhance the activity and to overcome the possible steric hindrance around the active site, trisiloxane, pentamethylene,[19] or silanes[20] have been used as spacers between the metallocene and support. Silanes have also been used in Ziegler–Natta systems as electron donors to increase the isotacticity of the polypropylene.[21]

Our aim was to investigate further the influence of the spacer molecules by preparing supported metallocene complexes using commercially available silanes, to analyze the surface complexes, and to do a limited number of initial tests of the olefin polymerization activity. The focus is thus placed on the properties of the catalyst material, rather than on the features of the polymer formed. Amino and mercapto silanes were chosen since they are commercially available and homogeneous catalyst complexes containing these ligands have been reported in the litterature.[22,23] For comparison, the metallocene complexes were also adsorbed directly on the untreated silica surface. The activities and polymer properties were compared with those obtained by using the homogeneous catalyst. In previous studies, the acid–base properties of silica[24,25] and the mechanism of the adsorption of silanes on silica[26] were evaluated. We have also reported the influence of substrate modification on the catalytic activity of metallocenes.[7] In the present work, the amount and the mechanism of the adsorption of metallocene on the untreated and the silane spaced silica support were studied. The effect of silane treatment on the catalyst activity of the supported metallocene in ethylene polymerization was of special interest.

The silica supported zirconium complexes were prepared using the following three different methods: (1) the metallocene (bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) or bis(cyclo-pentadienyl)zirconium chloride hydride (Cp_2ZrClH)) was directly adsorbed onto the silica support; (2) silica was treated with a silane coupling agent containing an appropriate ligand, NH_2 (γ-aminopropyltrimethoxysilane, $NH_2CH_2CH_2CH_2Si(OCH_3)_3$, APTMS) or SH ($\gamma$-mercaptopropyltrimethoxysilane, $SHCH_2CH_2CH_2Si(OCH_3)_3$, MPTMS) followed by adsorption of Cp_2ZrCl_2; (3) an alkylzirconium complex was prepared on the silica surface by using the hydrozirconation reaction.[27] Silica was first treated with vinyltrimethoxysilane ($CH_2{=}CHSi(OCH_3)_3$, VTMS) and then reacted with zirconocene chloride hydride (Cp_2ZrClH) to produce the alkyl zirconium supported complex $Cp_2Zr(C_2H_3TMS)Cl$.

The supported complexes were characterized using diffuse reflectance infrared spectroscopy (DRIFT), solid-state (^{13}C-CPMAS NMR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) to allow identification of the structure of the metallocene on the support surface. Direct current plasma atomic emission spectroscopy (DCP-AES) was used to determine the amount of zirconium on the support. Ethylene was polymerized with the supported complexes to determine their catalytic activity.

Experimental Section

Materials. γ-Aminopropyltrimethoxysilane ($NH_2CH_2CH_2CH_2Si(OCH_3)_3$) (APTMS, A-1110, OSi Specialities); γ-mercaptopropyltrimethoxysilane ($SHCH_2CH_2CH_2Si(OCH_3)_3$) (MPTMS, A-189, OSi Specialities); vinyltrimethoxysilane ($CH_2{=}CHSi(OCH_3)_3$) (VTMS, A-171, OSi Specialities); bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2, 98+%, Aldrich) or bis(cyclopentadienyl)zirconium chloride hydride (Cp_2ZrHCl, ~95%, Aldrich); and methylaluminoxane (MAO, 10% solution in toluene, Witco) were used as supplied. Ethylene (grade 3.5 from AGA) was purified by passing it through columns filled with 3-Å molecular sieves, BASF R3-11 copper catalyst and activated alumina. Porous silica powder (Grace Si, S8MY) was reported by the manufacturer to have an $A_{sp} = 303\ m^2/g$ and an average particle diameter of 70 μm. The silica powder was heat-treated at 420 °C at ambient atmosphere for 20 h before use. As reported previously,[7] the BET surface area after the thermal treatment is 372 m^2/g, pore volume 1.7 cm^3/g, and pore diameter 6–30 nm. According to Kaminsky[2] and Zhuravlev[26] the surface Brφnsted site density is then around 2.5 OH groups/nm^2, but lower values in the range of 1.4 OH groups/nm^2 has been reported for partially dehydroxylated silica.[27] Toluene (Lab Scan, AR) was dried by refluxing over sodium and benzophenone (Merck, >99%) until a blue ketyl was formed, then distilling under nitrogen.

Catalyst Preparation. *Adsorption of Cp_2ZrCl_2 onto Silica (Sil-CpZrCl).* Silica (2.28 g), toluene (30 mL), and Cp_2ZrCl_2 (125.4 mg) were stirred together under nitrogen at ambient temperature for 24 h. The solution was filtered off under nitrogen (via cannula), then the catalyst was washed with toluene (3 × 25 mL), followed by drying in a vacuum for 4 h (0.3 kPa, 50 °C). The same filtering, washing, and drying procedures were used for the preparation of all catalysts. The DCP analysis on the filtrate and washing liquids (total 400 mL) indicated that there was 21.2 mg of Zr, which is equivalent of 6.8 mg of zirconocene dichloride. The amount adsorbed was thus 0.18 mmol (Zr)/g silica.

Adsorption of Cp_2ZrHCl onto Silica (Sil-CpZrH). Silica (2.43 g), toluene (30 mL), and Cp_2ZrHCl (115.9 mg) were stirred together in a flask covered with aluminum foil (in the dark) under nitrogen at ambient temperature for 24 h. The separa-

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Table 1. Zirconium Content of the Supported Complexes Determined by DCP

supported complex	description	zirconium content (mmol/g)	site density (molecule (Zr)/nm^2)
Sil-ZrCp	Cp_2ZrCl_2 adsorbed onto silica	0.18 ± 0.02	0.29
Sil-ZrCpH	Cp_2ZrHCl adsorbed onto silica	0.18 ± 0.02	0.29
Sil-NHZrCp	Cp_2ZrCl_2 reacted with aminosilane treated silica	0.37 ± 0.03	0.60
Sil-SHZrCp	Cp_2ZrCl_2 reacted with mercaptosilane treated silica	0.57 ± 0.04	0.92
Sil-CH_2CH_2Zr	Cp_2ZrHCl reacted with vinylsilane treated silica	0.44 ± 0.04	0.71

tion procedure of Cp_2ZrHCl was the same as above and the DCP analysis showed 0.18 mmol (Zr)/g silica.

Preparation of Supported Metallocenes with Amino (Sil-NHCpZrCl) Groups. Silica (2.06 g), toluene (22 mL), and 1.0 g of γ-aminopropyltrimethoxysilane (APTMS) were stirred together under nitrogen for 16 h. The separation procedure was the same as above. Then a solution containing zirconocene dichloride (222.9 mg) in toluene (50 mL) was added to 2.06 g of the APTMS treated support and stirred under nitrogen for 24 h. Again the separation procedure was the same and the DCP analysis showed 0.37 mmol (Zr)/g silica.

Preparation of Supported Metallocenes with Mercapto (Sil-SHCpZrCl) Groups. Silica (2.29 g), toluene (22 mL), and 1 g of γ-mercaptopropyltrimethoxysilane (MPTMS) were stirred together under nitrogen for 16 h. The separation procedure was the same as above. Then a solution containing zirconocene dichloride (183.1 mg) in toluene (50 mL) was added to 1.09 g of the MPTMS treated support and stirred under nitrogen for 24 h. Again the separation procedure was the same and the DCP analysis showed 0.57 mmol (Zr)/g silica.

Preparation of the Alkylzirconium Supported Complex (Sil-C_2H_3CpZrH). Silica (2.1 g), toluene (22 mL), and 1 g of vinyltrimethoxysilane (VTMS) were stirred together under argon for 16 h. The separation procedure was the same as above. Then a solution containing zirconocene chloride hydride (88.4 mg) in toluene (30 mL) was added to 0.78 g of the VTMS treated silica and stirred in an aluminum foil covered flask (in dark) for 24 h. Again the separation procedure was the same and the DCP analysis showed 0.44 mmol (Zr)/g silica.

Polymerization Procedure. A polymerization reactor was filled with 300 mL of toluene and a suspension of the catalyst in toluene (Table 1) was added together with the appropriate amount of MAO. The amount of MAO introduced was varied to give n_{Al}/n_{Zr} ratios of 500, 1000, and 2000. Ethylene was introduced into the reactor at a partial pressure of 2.5×10^5 Pa and polymerization was carried out at 50 °C then terminated by acidic methanol. The blank reaction was done with the same conditions using only MAO for the reaction.

Characterization Techniques. *DCP.* The zirconium concentration was determined using direct current plasma atomic emission technique (DCP-AES) and a Spectra Span III B spectrometer (Spectrametrics, Inc.) at 343.8 nm. After each reaction of the metallocene with the support, the filtrate and washing solutions were diluted to 400 mL with toluene then analyzed for zirconium. The zirconium concentration obtained from the DCP analysis was subtracted from the initial concentration of zirconium added to the silica (silane spaced or untreated) to give the amount of zirconium adsorbed.

DRIFT. Samples were analyzed with a Bruker IFS 66 FTIR spectrometer in the wavenumber region 4000−400 cm^{-1}. Samples for DRIFT analysis were made by mixing approximately 15% w/w of calcined silica, silane treated silica, or catalyst with the background material KBr. The prepared sample was filled in the DRIFT sample cup by gentle tapping, then mounted on a Spectra Tech diffuse reflectance apparatus and scanned 100 times.

XPS. XPS spectra were obtained using a Perkin-Elmer Small Spot PHI 5400 ESCA spectrometer employing nonmonochromatic Mg Kα X-rays. The area analyzed had a diameter of ~1 mm. The base pressure in the spectrometer was typically 2×10^{-7} Pa and during measurement was 7×10^{-7} Pa.

A survey spectrum from 1 to 1100 eV was recorded for each sample, using 0.5-eV steps and 89.5 eV analyzer energy. Narrow scans for the C 1s, Cl 1s, N 1s, O 1s, Si 1s, and Zr 1s with a step of 0.1 eV and an analyzer energy of 35.75 eV were made. All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV to compensate the effect of surface charging. The samples were introduced into the analyzing chamber via a vacuum cell to avoid oxidation of the samples.

Solid-State 13^C-CPMAS NMR. Experiments were carried out using a Chemometrics CMX 270 Infinity NMR spectrometer. The parameters used were: 4.5 μs (90°) pulse (55 kHz r.f. field), 2.9 ms contact time, 5.0 s recycle delay, 15 000 transients, and 5.0 kHz MAS rotation frequency.

Gel Permeation Chromatography (GPC). The M_w of the polymers and the polydispersity (M_w/M_n) were measured at 140 °C by a Waters 150C GPC using 1,2,4-trichlorobenzene as the solvent. The columns were calibrated with narrow M_w polystyrene standards.

Differential Scanning Calorimetry (DSC). The melting point (T_m) of the produced polymers was measured using a Perkin-Elmer DSC 7 at a heating rate of 10 °C/min.

Results and Discussion

Zirconium Analysis. To determine the amount of metallocene adsorbed onto the silica (calcined or silane treated), DCP analysis of the toluene solution after adsorption of the metallocene was utilized to determine the amount of immobilized Cp_2ZrCl_2. The results (Table 1) indicate that both types of metallocenes adsorbed onto the calcined silica in amounts almost exactly the same as the amount added (0.18 mmol Zr/g silica). As ZrH reacts more readily with OH groups than ZrCl one would have expected a higher amount of Cp_2ZrClH to chemisorb than Cp_2ZrCl_2.[17] The same occupation of sites observed (0.29 OH/nm^2) arise, however, from incomplete addition of the catalyst.

When the silica was first treated with a silane the amount added was in excess of the surface hydroxyl groups but the amount adsorbed was not quantified. The amount of metallocene adsorbed increased, however, indicating that the metallocene indeed binds to the silane linker molecule. The reason for the growth is the increased amount of catalyst added since the chemisorption of metallocene is almost complete. Site densities (molecule(Zr)/nm^2) show (Table 1) that only a fraction (0.6−0.9 (Zr)/nm^2) of the active sites (the silanol, amine, or silane groups) are consumed through metallocene attachment.

DRIFT Analysis. DRIFT is a nondestructive technique that can be used to monitor the adsorption of compounds on the silica. In this work, DRIFT spectra of all of the supported complexes and intermediates were recorded in order to identify the surface species on the support. The DRIFT spectrum of calcined silica is given in Figure 1a. The sharp peak at 3747 cm^{-1} is due to isolated noninteracting silanol groups, i.e., Si−OH, while the weak peaks at 3670−3650 cm^{-1} are assigned as structurally inaccessible hydrogen-bonded

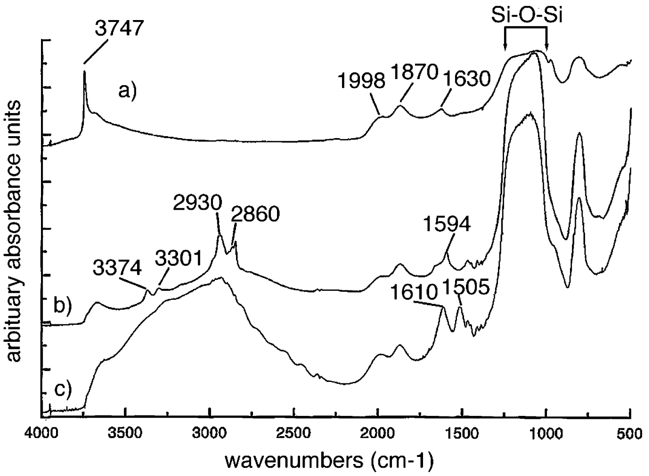

Figure 1. DRIFT spectra of (a) calcined silica, (b) silica treated with aminopropyltrimethoxysilane (Sil-NH_2), and (c) silica treated with aminopropyltrimethoxysilane followed by adsorption of Cp_2ZrCl_2 (Sil-NHCpZrCl).

OH groups.[28] At 1870 and 1998 cm^{-1} the Si−O−Si modes of silica itself are observed.[30]

When the two metallocenes were adsorbed onto the calcined silica the spectrum of the silica appeared to remain unchanged, with no cyclopentadiene stretches detected (not shown). Since some adsorption is expected to occur at the free SiOH sites a reduction in the intensity of the peak at 3747 cm^{-1} is observed. To confirm this, the area of the peak at 3747 cm^{-1} was determined and divided by the area of the peak at 1870 cm^{-1} (Si−O−Si overtones of silica). Murthy et al.[31] have found that the peak at 1870 cm^{-1} is the least affected by particle size of the sample and is the most suitable to be used as an internal standard. The values obtained were $A_{3747}/A_{1870} = 0.78$ for calcined silica, and $A_{3747}/A_{1870} = 0.54$ for both Sil-CpZrCl and Sil-CpZrH. This reduction in intensity indicates adsorption on some of the free Si−OH sites. Decomposition of the metallocene may also occur with the cyclopentadiene being removed. Collins et al.[11] have shown by ^1H NMR studies that during adsorption of ethylenebis(η^5-indenyl)zirconium, the bis(indenylethane) complex forms. In our case, it is not certain whether decomposition has occurred as the amount of metallocene on the surface may be too low for DRIFT to detect the cyclopentadiene groups.

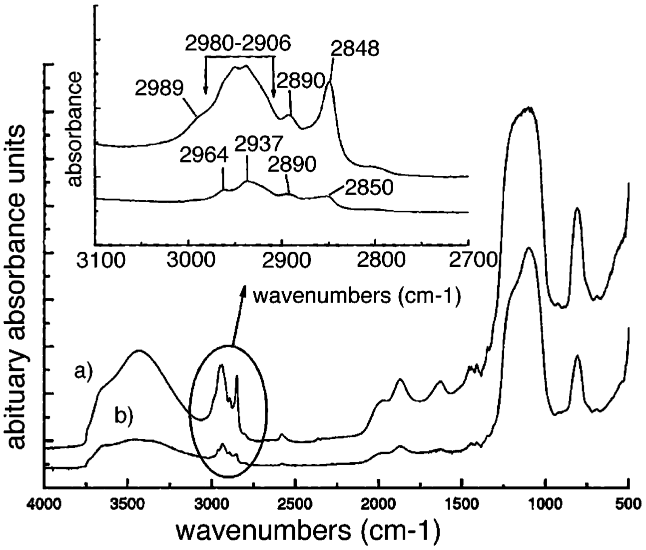

Figure 2. DRIFT spectra of (a) silica treated with mercaptopropyltrimethoxysilane (Sil-SH), and (b) silica treated with mercaptopropyltrimethoxysilane followed by adsorption of Cp_2ZrCl_2 (Sil-SHCpZrCl).

Table 2. Assignment of C−H Stretches for Silica Treated with Mercaptopropyltrimethoxysilane

C−H stretch	frequency (cm^{-1})
O−CH_3	2989 (asym CH_3)[a]
	2848 (O−CH_3)
	2954 (sym CH_3)
CH_2Si	2937 (asym)
$HSCH_2$	2890 (sym)
	2964 (asym)

[a] asym= asymmetric stretch, sym= symmetric stretch.

Silica treated with an amino and mercapto silane has been used previously to prepare platinum, rhodium, cobalt, or ruthenium supported complexes for catalyzing reactions such as hydrogenation, hydrosilylation, or isomerization.[29] The spectra of APTMS treated silica and subsequent catalyst, Sil-NHCpZrCl, are shown in Figure 1b and c, respectively. When the silane is adsorbed onto the silica, the peak at 3747 cm^{-1} has disappeared or diminished significantly due to the reaction of the hydrolyzable OCH_3 or the amino groups with surface Si−OH groups. The peaks at 3374 and 3301 cm^{-1} are the asymmetric and symmetric stretchings of the primary amine, respectively. The deformation mode of the NH_2 group is found at 1594 cm^{-1} and the stretching vibrations of the CH groups in the silane are observed at 2800−3000 cm^{-1}. Adsorption isotherms[26] have shown that the silane forms in excess porous multilayer siloxane gels on the silica. When Cp_2ZrCl_2 was adsorbed on the aminosilane treated silica (Figure 1c), two new NH stretches appeared at 1610 and 1505 cm^{-1}, which are assigned as NH_3^+ species. Primary amine salts have stretching vibrations in the region 2100−2800 cm^{-1} which were observed as a series of small broad bands between 2500 and 2800 cm^{-1}, indicating the formation of a $NH_3^+Cl^-$ salt during adsorption of the metallocene.[1]

Figure 2a and b display the DRIFT spectra for MPTMS treated silica and subsequent catalyst, Sil-SHCpZrCl, respectively. The peaks due to the SH (at 2550 cm^{-1}) and the C−H stretching vibrations (Table 2) were observed after silane treatment. After adsorption of the metallocene, the OCH_3 groups appear to have hydrolyzed further, as the peak at 2989 cm^{-1} has disappeared. The region between 2980 and 2906 cm^{-1} has now resolved into two peaks (2937 cm^{-1}, CH_2Si asymmetric stretch, and 2964 cm^{-1}, $HSCH_2$ asymmetric stretch). The silane signal is also attenuated due to the presence of the metallocene.

The spectra of VTMS treated silica and Sil-C_2H_3-CpZrH are shown in Figure 3a and b. As vinyltrimethoxysilane has adsorbed on silica (Figure 3a), strong peaks at 1602, 3027, and 3070 cm^{-1} due to the CH=

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Table 3. Binding Energies (eV) for Some Reference Materials and for Homogeneous Cp_2ZrCl_2 and Supported Complexes

sample	C $1s_{1/2}$	fwhm	O $1s_{1/2}$	fwhm	Si $2p_{1/2}$	fwhm	Cl $2s_{1/2}$	fwhm	Zr $3d_{5/2}$	fwhm	N 1s	fwhm	S $2p_{1/2}$	fwhm
Cp_2ZrCl_2 (homog.)	284.9						198.8		182.0					
Sil-CpZrH	284.6	3.5	532.7	2.9	103.3	2.9	196.7	8.0	183.1	4.5				
Sil-NH_2[a]	284.6	3.0	532.3	2.9	102.9	2.8					399.0	2.8		
Sil-NHCpZrCl	284.6	3.0	532.2	2.5	103.0	2.7	198.3	3.2	182.8	4.7	400.3	4.0		
$Cp_2Zr(NEt)_2$[b]	284.9								181.6		399.1			
Sil-SH[c]	284.6	3.2	532.4	2.2	103.0	2.5							163.3	2.7
Sil-SHCpZrCl	284.6	2.9	532.5	2.6	103.1	2.9			183.1	4.7			163.5	2.7
ZrO_2[d]									183.3					
Sil-CH=CH_2[e]	284.6	2.9	532.4	2.5	102.9	2.8								
Sil-C_2H_3CpZrH	284.6	3.2	532.7	2.8	103.1	2.9	198.8	4.0	182.7	4.7				
$Cp_2ZrClCH_3$[f]									181.2					
$Cp_2Zr(CH_3)_2$[f]									180.7					

[a] Silica treated with aminopropyltrimethoxysilane. [b] Ref 42. [c] Silica treated with mercaptopropyltrimethoxysilane. [d] Ref 43. [e] Silica treated with vinyltrimethoxysilane. [f] Ref 44.

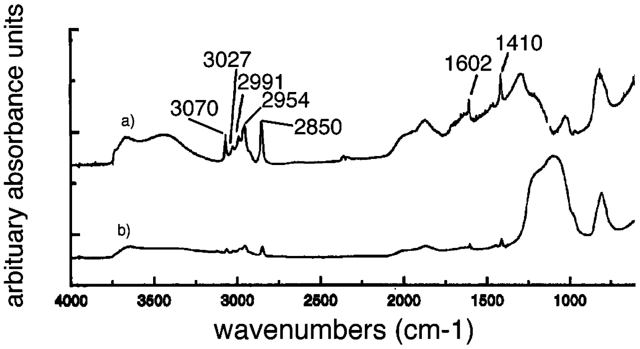

Figure 3. DRIFT spectra of (a) silica treated with vinyltrimethoxysilane (Sil-CH=CH_2) and (b) silica treated with vinyltrimethoxysilane followed by adsorption of Cp_2ZrHCl (Sil-C_2H_3CpZrH).

CH stretching are observed. The other C−H stretches (between 2800 and 3000 cm^{-1}) are due to the OCH_3 groups in the silane (see Table 2 for assignments). If Cp_2ZrClH has reacted with the vinyl groups on the silica surface, the intensity of the peaks at 1602, 3027, and 3070 cm^{-1} should be reduced. The spectrum of Sil-C_2H_3-CpZrH (Figure 3b), does show attenuation of the silane signals, but the double bond signals are still present. The metallocene is likely to have reacted with the outermost silane groups, leaving unreacted silanes underneath.

XPS and NMR Analysis. XPS is a more surface sensitive technique than DRIFT and gives some information on the nature of the surface species. Table 3 gives the XPS results for the supported metallocenes and a homogeneous metallocene. Zirconium metal was not detected by the XPS for Sil-ZrCp, probably due to the heterogeneous nature of the sample. The binding energy of the supported complexes was observed to be higher than that of the homogeneous Cp_2ZrCl_2, indicating interaction with either the silica surface or the silane layer on silica.

Zirconium metal was not detected by the XPS for Sil-ZrCp sample and therefore ^{13}C-CPMAS NMR studies were carried out for this catalyst (not shown). The spectrum confirms that the zirconene is attached to the silica support surface. One peak at 115 ppm was observed relating to the cyclopentadienyl (Cp) ring bonded to zirconium.[32] The adsorption seems to occur at least partly via isolated OH groups. It is difficult to confirm any other information than that from the experimental data available.

The binding energy for the zirconium in Sil-ZrCpH was close to that of silica supported $Et(Ind)_2ZrCl_2$ complex characterized by Atiqullah et al.[16] This suggests that the indenyl complex forms a zirconium cation, $[SiO]^-[LZrCl]^+$ (L = indenyl ligand), on the surface of the silica support. When comparing the Sil-CpZrCl and Sil-CpZrH, the latter complex reacts much more specifically with hydroxyl groups to form $Cp_2ZrCl{-}O{-}Si$.[17] Such species can be effectively activated even by small quantities of MAO.[17]

The carbon multiplex from the XPS spectra of Sil-NHZrCp shows a broad absorbance at 291.5 eV, which is assigned as the $\pi \rightarrow \pi^*$ shake-up satellite from the cyclopentadiene ring. Shake-up satellites are usually observed for systems containing unsaturation, especially aromatic systems.[33] Carbonate structures $(NH_2^-(HCO_3)^-)$ can also have binding energies in the same range but these are usually formed at pH values around 10.[34] The zirconocene complex is acidic, and therefore the conditions are not favorable for the formation of carbonates. To confirm that carbonates had not formed, aminopropyltrimethoxysilane was adsorbed onto silica at pH 10.8. No signal was found at 291.5 eV for this sample. The other supported complexes did not have the $\pi \rightarrow \pi^*$ shake-up satellite in their carbon multiplexes, but it has been observed for phenyl compounds adsorbed onto glass fibers.[35]

The nitrogen multiplex spectrum of Sil-NH_2 has only one signal with a binding energy of 399.9 eV, assigned as free amine. In the nitrogen multiplex of Sil-NH-CpZrCl, the curve can be fitted to display two nitrogen species at 400.3 and 401.9 eV. The shift at 400.3 eV is assigned as the Zr−N species or hydrogen-bonded amine, whereas the shift at 401.9 eV is assigned as a protonated amine (NH_3^+).[36] Table 3 shows that the binding energy of zirconium in Sil-NHZrCp compared to that of a homogeneous Zr−N compound is higher indicating that a $[Cp_2ZrNH_3]^+$ complex has formed. The XPS data do confim the DRIFT data that a changed amino species has formed during the adsorption of zirconene.

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Table 4. Ethylene Polymerization Behavior of the Homogeneous Cp_2ZrCl_2 in Solution

catalyst	n_{Zr} (μmol)	n_{Al}/n_{Zr}	yield (g)	activity (kg(PE)/mol(Zr)h)	M_w (g/mol)	M_w/M_n	T_m (°C)
Cp_2ZrCl_2[a]	0.3	2000	5.11	29 880	476 000	2.5	137.5
Cp_2ZrCl_2[a]	0.7	2000	4.63	16 550	482 000	2.5	136.8
Cp_2ZrCl_2[b]	1.0	1000	4.63	13 530	434 000	2.7	136.5
Cp_2ZrCl_2[b]	1.0	500	0.62	1810	415 000	2.4	136.3

[a] 30 min. [b] 20 min.

Table 5. Ethylene Polymerization Behavior of the Supported Metallocenes in Solution[a]

catalyst	n_{Zr} (μmol)	n_{Al}/n_{Zr}	yield (g)	activity (kg(PE)/mol(Zr)h)	M_w (g/mol)	M_w/M_n	T_m (°C)
Sil-CpZrCl	1.8	2000	4.22	4690	544 100	2.5	137.3
Sil-CpZrCl	1.8	1000	3.45	3830	508 400	2.4	137.0
Sil-CpZrCl	1.8	500	1.89	2100	429 600	2.3	138.6
Sil-NHCpZrCl	5.6	2000	4.70	1690	517 000	2.1	138.5
Sil-NHCpZrCl	5.6	1000	3.50	1260	517 400	2.5	138.1
Sil-NHCpZrCl	5.6	600	3.07	1110	498 500	2.2	137.6
Sil-SHCpZrCl	2.3	2000	0.83	730	451 300	2.3	141.4
Sil-SHCpZrCl	2.3	1000	0.91	800	476 600	2.3	138.2
Sil-SHCpZrCl	2.3	500	0.08	71	394 700	2.3	139.4
Sil-CpZrH	0.9	2000	4.98	11 070	500 600	2.3	138.6
Sil-CpZrH	1.1	1000	3.28	6070	447 500	2.3	138.1
Sil-CpZrH	1.8	500	5.07	5630	449 500	2.4	138.1
Sil-C_2H_3CpZrH	0.7	2000	4.87	14 760	474 300	2.4	140.9
Sil-C_2H_3CpZrH	1.3	1000	5.40	8180	456 000	2.4	138.0
Sil-C_2H_3CpZrH	2.2	500	6.23	5660	488 700	2.5	138.8

[a] Time = 30 min.

There is only a little change in the binding energy of sulfur upon addition of zirconene, but the zirconium binding energy has increased, suggesting that oxidation of the zirconene has occurred on adsorption rather than formation of a Zr−S bond.

The zirconium binding energy for the Sil-C_2H_3CpZrH sample is higher than that for the homogeneous analogue $Cp_2ZrClCH_3$ (Table 3). Additionally, the DRIFT did show vinyl groups to be still present on the surface which create an electron deficient environment for the zirconium increasing the binding energy further. Chlorine is still present on the surface, with a binding energy in the range for a chlorine attached to zirconium. We conclude that a $Cp_2ZrClC_2H_3$ complex is formed on the surface.

Ethylene Polymerization. As shown, XPS and DRIFT give some information on the types of species present on the silica surfaces after silane treatment and adsorption of the metallocene. However, the most important information needed is whether the complexes catalyze polymerization of olefin. All of the supported complexes and the homogeneous catalyst, Cp_2ZrCl_2, were used to polymerize ethylene. The metallocenes, Cp_2ZrCl_2 and Cp_2ZrClH, are expected to act similarly in the homogeneous reaction. The results of the homogeneous polymerization experiments are summarized in Table 4. The blank reaction carried out at the same conditions but using only MAO for the reaction did not show any activity.

All immobilized complexes displayed some catalytic activity (Table 5), with Sil-CpZrH and Sil-C_2H_3CpZrH giving the highest activities and yields. The activities of these two catalysts are rather high even compared with the homogeneous catalyst Cp_2ZrCl_2 being superior (Figure 4). Although several studies[12,37−39] have shown that it is common for zirconocenes L_2ZrR_2 (L = cyclopentadienyl, indenyl; R = CH_3, C_2H_5, Cl) to partially dissociate from the support when reacted with MAO, the obtained results do not support this view. To illustrate this view the activity and molar mass are plotted in Figure 4 as a function of MAO-loading (n(Al)/n(Zr)). As expected for supported catalysts,[13] the activity

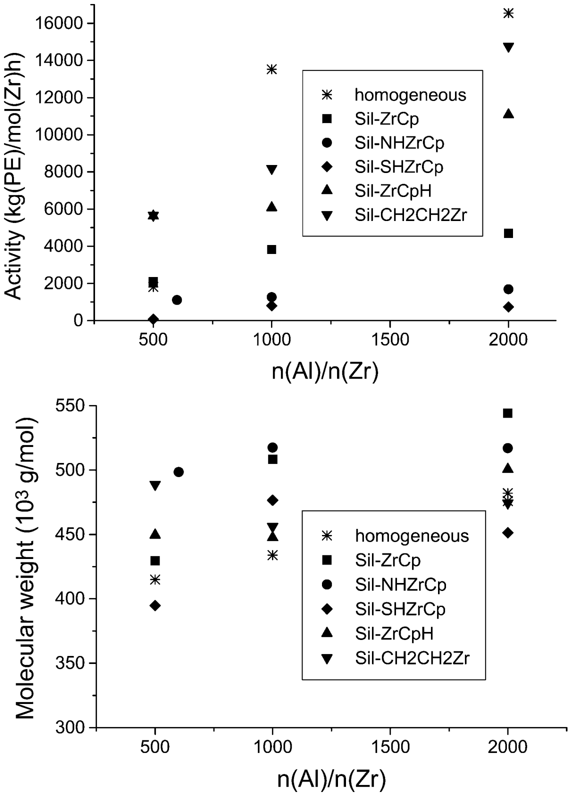

Figure 4. Catalyst activity and molar mass plotted as a function of the amount of MAO (n_{Al}/n_{Zr}) introduced in the polymerization slurry.

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is lower and the molar mass of the polymer produced is higher than when using the homogeneous catalyst. It is expected that the supported Sil-CpZrH catalyst had better activity than the Sil-CpZrCl. Since the Zr−H bond is more active toward the protolytic cleavage than a Zr−Cl or Zr−Cp bond (like Cp_2ZrMe_2[28]) a $Cp_2ZrCl-O-Si$ bond is expected to form with little, if any, side reactions. Such species can be effectively activated by even small quantities of MAO.[17] A further increase in activity was observed for Sil-C_2H_3CpZrH, indicating the complex formation which allows active centers to be available for the polymerization. Vinylsilane is an electron donor and can thus also contribute to the polymerization.

The mercapto and amino supported zirconium complexes gave limited activity and it seems that the sulfur is poisoning the catalyst, while the amino catalyst is only activated at exceedingly high catalyst loadings. For these two catalysts the silane has inhibited polymerization and deactivated the metal centers.[13] Soga et al.[40] have also obtained only trace amounts of polymer when they formed a catalyst by combining mercaptosilane with the metallocene in solution followed by reaction with an alkylaluminum complex. The deactivation may be due to an adsorption of the catalyst into the siloxane gel.

Overall, the molar mass seems to slightly increase with an enhanced amount of MAO present. However, as pointed out by one referee, the dependency is not statistically significant. The polydispersity (M_w/M_n) remained roughly constant at 2.4 ± 0.1. This is a typical value for polymers produced with the metallocene catalysts.[41] The observed melting temperatures ($137 < T_m < 141$ °C) of the polymers were high, indicating the formation of linear high-density polyethylene.

The polymerization mechanism is further illustrated as the yield plotted against the activity in Figure 5. Considering that the reaction time was kept constant (30 min) the following conclusions may be drawn. (1) For Sil-NHCpZrCl, Sil-CpZrCl (including Sil-SHCpZrCl), and Sil-CpZrH different constant slopes were found, although the yield with Sil-SHZrCp was exceedingly small (Figure 5a). A linear relationship was also found for the homogeneous Cp_2ZrCl_2 catalyst up to a maximum yield of about 5 g (PE) corresponding to an activity of about 13 000 kg(PE)/mol(Zr)h. For these systems the amount of zirconocene remains constant when the relative amount, n_{Al}/n_{Zr}, of MAO is increased. (2) At enhanced activities (>5000 kg(PE)/mol(Zr)h) the yield becomes independent of the activity. The yield of Sil-NHCpZrCl does, however, not reach this level. The constant yield becomes more obvious when the relationship is identified for the three constant MAO loadings. Then the yield−activity dependency for $n(Al)/n(Zr) = 500$ remains linearly dependent (Figure 5b). Moreover the slope roughly corresponds to that found for the Sil-ZrCp catalyst but is more than double the slope produced by the homogeneous catalyst (Figure 5a). However, for $n_{Al}/n_{Zr} = 2000$ (except for the Sil-SHZrCp catalyst) a constant plateau value is found at a yield of about 5 g (PE). This plateau equals the plateau found for the homogeneous catalyst for activities exceeding 13 000 kg(PE)/mol(Zr)h (Figure 5a). Note that the supported catalyst give yields corresponding to that of the homogeneous catalyst at only a fraction of the activity of the latter one! The kinetics (activity) and the extent (yield) of the polymerization reaction thus clearly differ for supported and homogeneous catalysts. The interrelation (slope) is strongly dependent on the type of catalyst immobilization, the extent of the reaction is not. In line with this observation (again excluding the Sil-SHZrCp catalyst) two plateaus may be deducted for the $n_{Al}/n_{Zr} = 1000$ systems (Figure 5b). At low activities the plateau remains at 3.5 g (PE), but when the activity exceeds 7000 kg(PE)/mol(Zr)h the plateau value is increased to the value of the $n_{Al}/n_{Zr} = 2000$ systems. The extent (yield) of the polymerization reaction becomes (for all catalysts) independent of the kinetics (activity) for different levels of super-saturation of MAO.

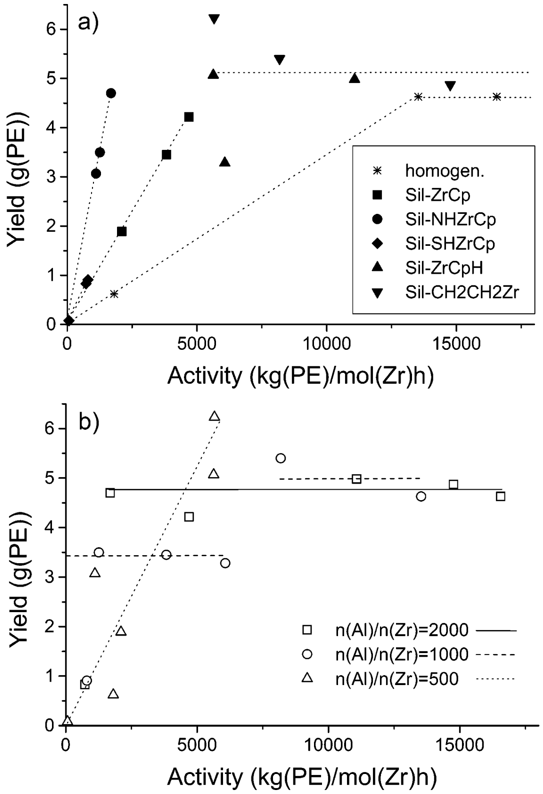

Figure 5. Yield plotted against activity for all the prepared catalysts: (a) for each catalyst, and (b) for different constant MAO loadings.

Conclusions

Metallocenes could be successfully supported on calcined silica treated with a bifunctional silane spacer molecule. DRIFT and XPS were shown to provide valuable information on the structure of the silane and the type of zirconium species on the surface.

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Initial catalytic tests showed that all complexes were catalytically active. The activity was observed to be dependent on the nature of the catalyst−spacer pair.

When aminosilane were used as a spacer for the metallocene (Cp_2ZrCl_2) the catalytic activity was observed to decrease as compared with the catalyst directly supported on the silica support and furthermore the homogeneous catalyst. Mercaptosilane appears to poison the catalyst.

Cp_2ZrClH or the vinyl silane spaced catalyst was observed to give a higher activity, but still lower than that of the homogeneous catalyst, Cp_2ZrCl_2.

The polyethylene molar masses (M_w) obtained by using supported catalysts were in general higher than those obtained using the homogeneous catalyst. This, together with the lower activity, supports the experimental evidence that the supported catalyst remained (at least initially) adsorbed in the presence of MAO.

Plotting the extent (yield) against the speed (activity) of the polymerization reaction reveals that the immobilization reduces the kinetics, but not the extent of the reaction.

The extent (yield) of the reaction is primarily dependent on the MAO loading up to a saturation limit. Above this limit the yield becomes independent of the reaction kinetics (and the type of catalyst) at a constant MAO ($n(Al)/n(Zr)$) level.

Acknowledgment. MSc Tom Eklund is thanked for technical support. The Graduate School of Materials Research (GSMR) and the Materials Structure Research Program (MATRA) of the Academy of Finland are acknowledged for funding the research.

CM0111229