Silica-supported zirconocene catalysts: Preparation, characterization and activity in ethylene polymerization

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Abstract

Supported catalysts for ethylene polymerization have been prepared by interaction of Cp_2ZrX_2 ($Cp = \eta^5\text{-}C_5H_5$, $X = Cl$ or CH_3) with silica chemically modified by $(CH_3)_3SiCl$ (TMCS) or trialkylaluminium compounds AlR_3 ($R = C_2H_5$ (TEA) and $^iC_4H_9$ (TIBA)). The interactions between the modificators and the silica surface have been examined by ^1H solid-state MAS NMR spectroscopy, DRIFTS and chemical analysis. The $Cp_2Zr(CH_3)_2/SiO_2$–TMCS catalyst showed a fairly high activity in ethylene polymerization (30–300 kg PE(mol $Zr \cdot h \cdot bar)^{-1}$) even in the absence of any cocatalysts specially added. The addition of the cocatalyst (MAO or TIBA) led to a further increase in the activity of the supported catalysts. Polyethylene obtained with the $Cp_2Zr(CH_3)_2/SiO_2$–TMCS catalyst without any cocatalyst consisted of uniform polymer particles of a spherical shape replicating that of the silica particles, whereas the shapeless aggregates of finely dispersed polymer particles similar to those usually obtained with homogeneous systems were produced with the same supported catalyst in the presence of the MAO cocatalyst. © 1998 Elsevier Science B.V.

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1. Introduction

Zirconocenes, Cp_2ZrX_2 ($Cp = \eta^5\text{-}C_5H_5$ or its substituted analogs, $X = Cl$ or CH_3), activated with methylaluminoxane (MAO) are among the most effective homogeneous catalysts for production of polyolefins [1]. The de- termined work has been done to immobilize zirconocenes on carriers (for a few important patents, see Refs. [2–8]) [9–16]. The catalysts prepared by supporting Cp_2ZrX_2 on SiO_2, Al_2O_3 or $MgCl_2$ were usually employed in the slurry process with MAO as a cocatalyst in liquid phase. Compared to polymerizations with homogeneous systems, the polymers produced over the supported zirconocene catalysts showed higher molecular weights and higher melting

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points as well as the improved particle morphology [11–15]. In addition, in the case of Al_2O_3 and $MgCl_2$ employed as carriers, the immobilized zirconocenes could be easily activated with a relatively small amount of MAO or even by common alkylaluminiums instead of MAO [16]. Zirconocenes supported on unmodified SiO_2 showed minor polymerization activity probably due to the protonolysis of Cp_2ZrX_2 by surface hydroxyl groups. More recently, Soga et al. [12] found that the use of SiO_2 pretreated with MAO caused a marked increase in the activity of supported catalysts, most of the MAO being consumed to scavenge surface silanols.

We have prepared the supported zirconocene catalysts using silica dehydroxylated with more common chemical agents such as trimethylchlorosilane $(CH_3)_3SiCl$ (TMCS) or AlR_3 $(R = C_2H_5$ (TEA) or $^iC_4H_9$ (TIBA)) prior to supporting Cp_2ZrX_2. In this paper, we describe the preparation of these catalysts and their use in the polymerization of ethylene.

2. Experimental

2.1. Materials and methods

Solvents (*n*-pentane, *n*-hexane, toluene) and gases (ethylene, hydrogen, argon) were purchased from commercial sources and purified according to the usual procedures. SiO_2 (Davison, Grade 952; 310 m^2 g^{-1}) was calcined at 400°C for 2.5 h in air and then dehydroxylated at 700°C (3 h, 10^{-2} bar). $Cp_2Zr(CH_3)_2$ and Cp_2ZrCl_2 were prepared according to the literature [17]. Commercial TMCS was refluxed over molecular sieves under Ar atmosphere, degassed by repeated freeze–thaw cycles, distilled by a trap-to-trap procedure and then stored in vacuo. TEA and TIBA were taken as the 0.15 and 0.18 M solutions in *n*-hexane, respectively. MAO was donated from Witco, Berghamen as a 1.8 M solution in toluene and used without further purification. Air-sensitive materials were handled and stored under vacuum in all-glass

systems with breakable partitions [18] to prevent them from contact with air.

2.2. Preparation of the modified silica gel

2.2.1. Modification by TMCS

1.5–10 g of dehydroxylated SiO_2 was exposed to the TMCS vapor (a 5–10 fold excess of TMCS compared to the content of surface silanols was used) at 130 or 325°C for 24 h in a sealed ampoule. The resulting SiO_2–TMCS(130) or SiO_2–TMCS(325) sample was evacuated at 150–250°C for 2 h. The procedure was twice repeated, if necessary.

2.2.2. Modification by AlR_3

A solution of TEA or TIBA in hexane (10 ml) was added to 2 g of dehydroxylated SiO_2 suspended in 10 ml of hexane at −10°C under vigorous stirring. The gas evolution was observed at the first moment. The mixture was left at 20°C for 24 h. Then, the solid product SiO_2–AlR_3 was separated by decanting, washed up with hexane and dried in vacuo at 60°C for 2 h.

2.3. Catalyst preparation

In a typical experiment, 0.35 mmol of $Cp_2Zr(CH_3)_2$ (0.07 M solution in pentane or hexane) was added to the suspension of 1.5 g of support in 5 ml of pentane (hexane) at −10°C under vigorous stirring. The mixture was kept at 20°C for 20 h in the dark. Then, the solid fraction was separated, washed up thoroughly with pentane (hexane) and dried in vacuo. In the case of Cp_2ZrCl_2 employed instead of $Cp_2Zr(CH_3)_2$, the supported catalyst was prepared similarly, except that toluene was used as a solvent.

To prepare an impregnated metallocene catalyst by the incipient-wetness technique, 0.25 mmol of $Cp_2Zr(CH_3)_2$ (0.05 M in pentane) was added to 0.8 g of SiO_2-TMCS(325) suspended in 4 ml of pentane under stirring. The mixture was left at room temperature for 15 min and the solvent was evaporated in vacuo. The impreg-

nated support was dried in vacuo at 25°C for 30 min.

2.4. Sample characterization

The contents of Zr and Al in the supported catalysts were measured using a HCP-IES spectrometer with the accuracy of ± 0.01 wt%. Cl contents of the support were determined by X-ray fluorescence spectroscopy (WRA instrument with a W anode of X-ray tube). Diffuse reflectance FT-IR (DRIFT) spectra of the powder supports were recorded using a Bruker IFS 113-V instrument in a vacuum-tight cell, containing 80–100 mg of the sample. ^{1}H MAS NMR spectra of the supports were obtained using a Bruker MSL-400 spectrometer at 400.13 MHz. Spectra were recorded at ambient temperature with the pulse duration of 5 μs and the recycle time of 5 s; the number of scans varied from 200 to 800. Prior to the spectra recording, weighed samples were transferred in vacuo into glass tubes. After sealing, the tubes were placed into a quartz rotor of the Andrew type which was used for sample rotation at about 3 kHz. Chemical shifts were determined with respect to an external tetramethylsilane with ± 0.2 ppm accuracy. If necessary, the experimental spectra were deconvoluted into individual components using Bruker MSL software. The intensities of various NMR lines were determined using linear background substraction and integration of peak areas. The concentrations of protons were obtained from integrated intensities of the spectra peaks by comparing them with the peak in the spectrum of a standard silica sample.

2.5. Polymerization of ethylene

For the polymerization of ethylene, a 200 ml stainless steel autoclave was filled with 70 ml of hexane or toluene and 80–120 mg of the solid catalyst. If necessary, a solution of a cocatalyst (MAO in toluene or TIBA in hexane) was added. Polymerization was carried out at 80°C and constant pressure of 10 bar for 1 h.

3. Results and discussion

3.1. Elemental analysis, DRIFT and ^{1}H MAS NMR

It is well-known that heating SiO_2 in vacuum at temperatures as high as 700°C removes the majority of the surface OH groups [19]. Figs. 1 and 2 present DRIFT and ^{1}H MAS NMR spec-
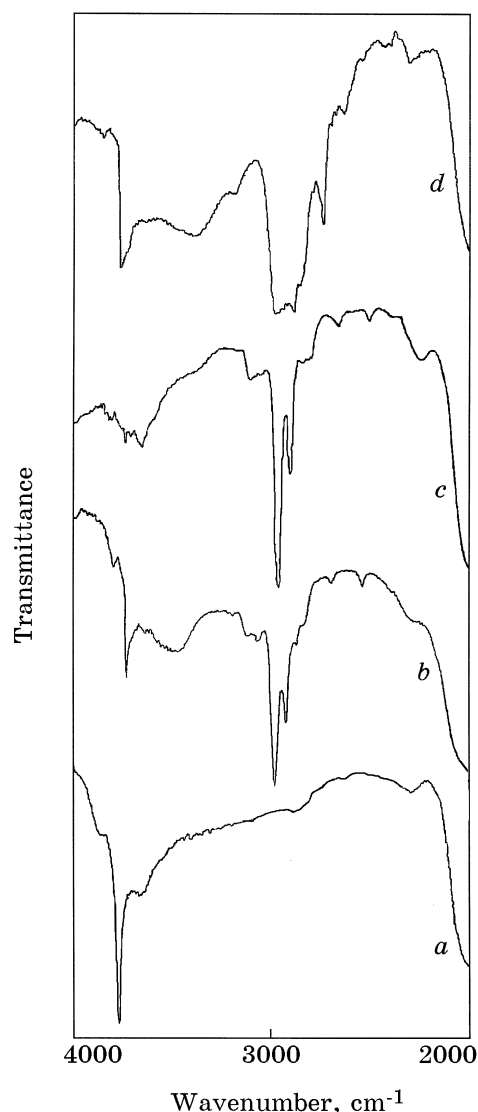

Fig. 1. DRIFT spectra of (a) original silica sample, (b and c) after silylation by TMCS vapor at 130 (b) and 325°C (c) and (d) after treatment with a TIBA solution.
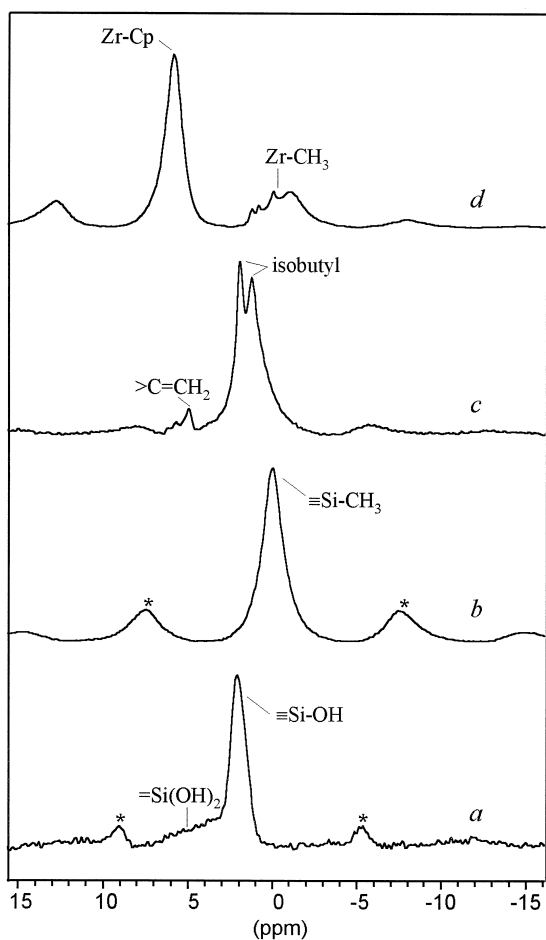
Fig. 2. Solid-state ^{1}H NMR MAS spectra of (a) original silica, (b) after silylation by TMCS vapor at 325°C, (c) after treatment with a TIBA solution and (d) after Cp$_2$Zr(CH$_3$)$_2$ adsorption on the silica sample a. Asterisks denote the spinning sidebands.

tra recorded for silica used to prepare the catalysts. DRIFT spectrum of a silica sample pre-evacuated at 700°C (Fig. 1a) exhibits a sharp band at 3750 cm^{-1}, corresponding to free surface OH groups (silanols) and a broader feature with maximum at 3640 cm^{-1} due to adjacent OH groups located inside silica globules [20]. Similarly, the ^{1}H MAS NMR spectrum (Fig. 2a) could be deconvoluted into two contribution peaks. One of them is a relatively narrow peak at $\delta \approx 1.8$–2.0 ppm, attributable to free silanols [21] and another is a broader Lorentzian centered at ca. 4.5 ppm which may be assigned to the internal OH groups [22]. The integrated area

of the whole spectrum indicates that the silica sample evacuated at 700°C contains $2.8 \cdot 10^{20}$ protons per g of SiO$_2$. This H content corresponds to the total concentration of OH groups of 0.46 mmol OH $\cdot$ g^{-1} or 0.9 OH group $\cdot$ nm^{-2} which is close to that of 1.1–1.2 OH group $\cdot$ nm^{-2} reported in Ref. [19]. Since the relative contribution of the ca. 2 ppm peak assigned to the internal OH groups accounts for ca. 75% of the total peak area, the concentration of free silanols may be estimated as ca. 0.35 mmol OH $\cdot$ g^{-1}.

After further treatment of the support with TMCS vapor at 325°C (Fig. 1c), the infrared band at 3750 cm^{-1} from external OH groups almost disappears, while the internal OH band (3640 cm^{-1}) is not noticeably reduced in intensity. In addition, the bands at 2970 and 2910 cm^{-1}, representing the asymmetric and symmetric CH$_3$ stretching vibrations appear in the spectra. The silylation at 130° (Fig. 1b) causes a similar but not so dramatic change in intensity of the silanol OH band which is reduced in intensity to about one third of its original value. The ^{1}H MAS NMR spectrum of silica treated with TMCS at 325°C (Fig. 2b) exhibits a single peak at $\delta \approx 0$ ppm which belongs to protons of the methyl groups. The ^{1}H spectrum of SiO$_2$-TMCS (130) sample is very similar to that of SiO$_2$-TMCS(325) except for that the peak area become smaller in the former case; the residual OH signal is not observed in this spectrum, probably, due to its obscuring by the intense resonance arising from Si(CH$_3$)$_3$ moieties. The concentrations of trimethylsilyl groups found by means of ^{1}H MAS NMR are 0.37 and 0.23 mmol $\cdot$ g^{-1} for SiO$_2$-TMCS(325) and SiO$_2$-TMCS(130), respectively. These data allow the conclusion that the free silanols are totally substituted by -Si(CH$_3$)$_3$ groups under the action of TMCS vapor at 325°C according to the equation:

$$\equiv Si-OH + (CH_3)_3SiCl$$

$$\rightarrow \equiv Si-O-Si(CH_3)_3 + HCl \qquad (1)$$
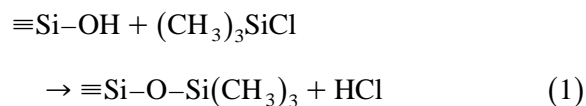
(hereafter $\equiv$Si is a silicon atom on the silica surface). Probably, only internal OH groups which are inaccessible for any reactants do not interact with TMCS at the temperature as high as 325°C. On the contrary, the silylation temperature of 130°C seems to be too low to remove the most of the external OH groups. It is worth noting that no detectable amount of chlorine appears in the support as a result of the treatment of silica with TMCS (the Cl content of the silica samples was ≤ 0.1 wt% both before and after silylation).

Aluminium alkyls are known to react with accessible OH groups of silica at room temperature to form surface $\equiv$Si–O–AlR$_2$ groups and to evolve alkane RH [10]. Accordingly, the treatment of silica with the TIBA solution (Fig. 1d) caused intense non-resolved CH stretching bands (3000–2800 cm^{-1}) and a reduction of the silanol OH band (3750 cm^{-1}) intensity, although the latter change was not so dramatic as that after high-temperature silylation. The corresponding solid-state ^{1}H MAS NMR spectrum recorded after the treatment of silica with the TIBA solution (Fig. 2c) contains no distinct peak at $\delta \approx 2.0$ ppm attributed to $\equiv$Si–OH groups; intense signals at $\delta = 0.9$ and 1.5 ppm tentatively assigned to methyl, methylene and methyne protons of isobutyl groups bonded to aluminium are observed instead (a weak feature at $\delta = 4.6$ ppm may belong to physically adsorbed isobutene). In our case, the quantity of the adsorbed TEA (0.63 mmol $\cdot$ g^{-1}) or TIBA (0.50 mmol $\cdot$ g^{-1}), as determined by Al analysis of the SiO$_2$–AlR$_3$ samples, was somewhat higher than the amount predicted from the stoichiometry '$\equiv$Si–OH:AlR$_3$ = 1:1' and taking into account the silanol content measured by NMR (0.35 mmol $\cdot$ g^{-1}). It is possible that TEA and TIBA also react with the siloxane bonds to form surface $\equiv$Si–O–AlR$_2$ and $\equiv$Si–H groups and to evolve ethylene or isobutene [23].

The zirconocenes Cp$_2$ZrX$_2$ were adsorbed on the silica surface as described in Section 2. Dimethyl zirconocene is adsorbed on the unmodified SiO$_2$ pre-evacuated at 700°C in the quantity, 0.32 mmol Zr $\cdot$ g^{-1}, which is closed to the content of accessible free $\equiv$Si–OH groups (0.35 mmol OH $\cdot$ g^{-1}). Compared with the original sample, the most remarkable changes in the ^{1}H MAS NMR spectrum of the silica treated with a Cp$_2$Zr(CH$_3$)$_2$ solution are the absence of the $\equiv$Si–OH resonances and the appearance of Zr–Cp and Zr–CH$_3$ resonances at $\delta = 5.7$ and -0.17 ppm, respectively (the small peaks at 0.7 and 0.9 ppm may be attributed to the solvent (*n*-hexane) physisorbed on the silica) (Fig. 2d). Based on these observations and by analogy with the known reaction of isostructural complexes of Cp$_2$MX$_2$ (M = Ti or Th) [24,25], dimethyl zirconocene may be supposed to interact with surface silanol groups of SiO$_2$ to form 'μ-oxo-like' complexes:

$$\equiv\text{Si–OH} + \text{Cp}_2\text{Zr(CH}_3\text{)}_2$$
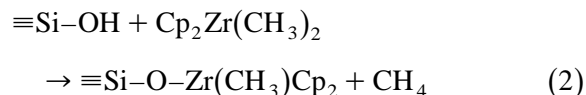
$$\rightarrow \equiv\text{Si–O–Zr(CH}_3\text{)Cp}_2 + \text{CH}_4 \qquad (2)$$

However, the Zr–Cp resonance in the ^{1}H MAS NMR spectrum of the Cp$_2$Zr(CH$_3$)$_2$/SiO$_2$ sample is much more intense in comparison with Zr–CH$_3$ resonance than that expected for $\equiv$Si–O–Zr(CH$_3$)Cp$_2$ complexes (Zr–Cp:Zr–CH$_3$ = 10:3). This discrepancy indicates that the reaction in Eq. (2) does not a single way for decomposition of Cp$_2$Zr(CH$_3$)$_2$.

The substitution of OSi(CH$_3$)$_3$ or OAlR$_2$ groups for OH groups of silica suppresses the adsorption of zirconocene (Table 1). Samples with a very low zirconium content of ca. 0.014 mmol Zr $\cdot$ g^{-1} were prepared by supporting Cp$_2$Zr(CH$_3$)$_2$ onto SiO$_2$-TMCS(325) followed by a long-time extraction of the solid with pentane. Even lower concentrations of zirconium (0.004 mmol Zr $\cdot$ g^{-1}) was produced when hexane containing ca. 3 wt% of toluene was used instead of pentane. A decrease in the silylation temperature from 325 to 130°C caused a substantial increase in the adsorption of zirconocene (up to 0.4 mmol Zr $\cdot$ g^{-1}). The probable reason is the interaction of zirconocene with the silanols which remained unsubstituted during the silylation at lower temperature. The

Table 1

Composition and ethylene polymerization[a] data for $Cp_2Zr(CH_3)_2$/modified SiO_2 catalysts

Run No.	Modificator[b]	Surface ligand	Content (mmol · g^{-1})		Yield (g PE · (g cat)$^{-1}$)	Activity (kg PE · (mol Zr · h · bar)$^{-1}$)
			Surface ligands	Zr		
1	none	-OH	0.46	0.32	traces	—
2	TMCS	-SiMe$_3$	0.37	0.014	4.2	32
3	TEA	-OAlEt$_2$	0.63	0.14	6.0	4.6
4	TIBA	-OAl^{i}Bu$_2$	0.50	0.11	3.8	3.6

[a] Polymerization at: temperature, 80°C; ethylene pressure, 10 bar; *n*-hexane, 70 ml; polymerization time, 1 h; quantity of catalyst, 80–120 mg; without cocatalyst.
[b] TMCS = trimethylchlorosilane; TEA = triethylaluminium; TIBA = tri(isobutyl)aluminium.
[c] The total concentration of surface OH groups including free silanols and internal hydroxyls in a 75:25 molar ratio.

adsorption of $Cp_2Zr(CH_3)_2$ on SiO_2–AlR_3 is one third of that on the unmodified silica but higher by an order of magnitude than that on SiO_2–TMCS(325) (Table 1). The latter may indicate that $Cp_2Zr(CH_3)_2$ interacts with the surface ≡Si–O–AlR_2 groups, as well as with the unsubstituted silanols.

3.2. Catalytic activity

Table 1 compares the results of ethylene polymerization with $Cp_2Zr(CH_3)_2$ adsorbed on both the unmodified and modified silica. The $Cp_2Zr(CH_3)_2$/SiO_2–TMCS(325) catalyst, even without cocatalyst, demonstrates a high activity of up to 32 kg PE · (mol Zr · h · bar)$^{-1}$ (Table 1, run 2), whereas the sample of $Cp_2Zr(CH_3)_2$/SiO_2 gives only a polymer trace under these conditions (Table 1, run 1). The activity of $Cp_2Zr(CH_3)_2$/SiO_2–AlR_3 catalysts (Table 1, runs 3 and 4) is far inferior to those of $Cp_2Zr(CH_3)_2$/SiO_2–TMCS(325) catalysts.

Since the catalyst prepared by supporting $Cp_2Zr(CH_3)_2$ onto silylated SiO_2 exhibited the highest activity, it was investigated in more detail by varying the conditions of the catalyst preparation as well as the polymerization conditions. The results are summarized in Table 2. The samples with the lowest Zr content obtained by adsorption of zirconocene on the completely silylated silica (catalysts 1 and 2) possess the highest activity (Table 2, runs 1–4). The catalytic activity of the silylated

zirconium-free silica was measured in a special experiment: in this case the polymer was not formed. The catalysts obtained with a partially silylated silica (catalyst 3) or prepared by incipient wetness impregnation (catalyst 4) have a Zr content which is higher by an order (catalyst 3) or a couple of orders (catalyst 4) of magnitude than that of catalyst 2, but give almost the same amount of polymer as 2. By comparing catalyst 1 with catalyst 3 (Table 2, runs 1 and 6), the extra amount of zirconocene adsorbed on

Table 2

Data on ethylene polymerization[a] catalyzed by $Cp_2Zr(CH_3)_2$/SiO_2–TMCS (TMCS = trimethylchlorosilane)

Run No.	Catalyst[b]	Zr (wt%)	Yield (g PE·(g cat)$^{-1}$)	Activity (kg PE· (mol Zr·h·bar)$^{-1}$)
1	1	0.13	4.2	32
2[c]	1	0.13	6.0	46
3[d]	1	0.13	3.9	30
4	2	0.04	10.4	304
5	2[e]	0.04	5.7	191
6	3	0.40	9.2	24
7	4	4.00	11.3	2.5

[a] Polymerization at: temperature, 80°C; ethylene pressure, 10 bar; *n*-hexane, 70 ml; polymerization time, 1 h; quantity of catalyst, 80–120 mg; without cocatalyst.
[b] (1) $Cp_2Zr(CH_3)_2$/SiO_2–TMCS(325); (2) catalyst (1) extracted with hexane containing 3% of toluene; (3) $Cp_2Zr(CH_3)_2$/SiO_2–TMCS(130); (4) $Cp_2Zr(CH_3)_2$ (imp.)/SiO_2–TMCS(325) prepared by incipient wetness impregnation; SiO_2–TMCS(325) and SiO_2–TMCS(130) stand for silica treated by TMCS at 325 and 130°C, respectively.
[c] Polymerization conducted using toluene as a solvent instead of hexane.
[d] Polymerization conducted in the presence of H$_2$ (4 bar).
[e] Catalyst 2 after exposure to air for 15 min.

SiO_2–TMCS(130) may be assumed to react with OH groups of the support, which remain unsubstituted, to form inactive Zr complexes. In regard to catalyst **4**, dimethyl zirconocene supported on the silylated silica by the incipient-wetness technique should be liberated into the solution under polymerization conditions, except for a very small amount of the complex (only 1% of the total) which is irreversibly adsorbed. It is well known that the dissolved $Cp_2Zr(CH_3)_2$ shows no polymerization activity in the absence of MAO or AlR_3. Since we tested catalyst **4** without any cocatalysts, the irreversibly adsorbed zirconocene species are, probably, responsible for the catalytic activity. The comparison of catalysts **2** and **4** (Table 2, runs 4 and 7) further suggests that some sites, which can activate the supported zirconocene species, are present on the surface of silylated silica. Therefore, a direct bonding between support and metallocene might be necessary for the polymerization activity of the discussed systems in the absence of any cocatalyst.

Some variations in the procedures for the polymerization tests, such as the use of toluene as a solvent instead of hexane (Table 2, run 2) or addition of H_2 (Table 2, run 3), only slightly affect the activity of catalysts **1** and **2**. It is interesting to note that a short time (15 min) exposure of the catalyst **2** to air does not decrease its activity so much (Table 2, runs 4 and 5). This may be attributed to the fact that the hydrophobic surface of silylated silica adsorbs the moisture rather slowly, which decomposes the surface zirconocene species.

Table 3 presents the results of ethylene polymerization conducted with the supported $Cp_2Zr(CH_3)_2$-based catalysts in combination with MAO. The introduction of a relatively small excess of MAO corresponding to the Al:Zr ratio of 100 into the polymerization medium causes ca. 30 times increase in the activity of $Cp_2Zr(CH_3)_2$/SiO_2–TMCS catalyst (Table 3, runs 1 and 2). $Cp_2Zr(CH_3)_2$ supported on unmodified SiO_2 was also found to be activated by MAO (Table 3, runs 3 and 4). Thus, at least a part of dimethyl zirconocene, when reacted with the surface OH groups is deactivated reversibly. However, at the similar Al:Zr ratio, the activity of the catalytic system $Cp_2Zr(CH_3)_2$/SiO_2 + MAO is lower by an order of magnitude than that of the $Cp_2Zr(CH_3)_2$/SiO_2–TMCS + MAO system. The homogeneous catalytic system composed of $Cp_2Zr(CH_3)_2$ and MAO was also tested for reference (Table 3, runs 5 and 6). At 70°C and the Al:Zr ratio of 100 the activity of the homogeneous system $Cp_2Zr(CH_3)_2$ + MAO was one third that of the **1** + MAO catalyst tested at 80°C and the same Al:Zr ratio (cf. runs 2 and 6 in Table 3).

The similarity between the homogeneous $Cp_2Zr(CH_3)_2$ + MAO and heterogeneous $Cp_2Zr(CH_3)_2$/SiO_2–TMCS + MAO systems is

Table 3
Effect of MAO on ethylene polymerization[a] in the presence of $Cp_2Zr(CH_3)_2$-based catalysts

Run No.	Catalytic system	Zr^b (mol × 10^6)	Al:Zr molar ratio	Activity (kg PE · (mol Zr · h · bar)$^{-1}$)
1	$Cp_2Zr(CH_3)_2$/SiO_2–TMCS(325)^c (**I**)	1.5	0	46
2	**I** + MAO	1.0	100	1200
3	$Cp_2Zr(CH_3)_2$/SiO_2 (**II**)	14.2	0	—
4	**II** + MAO	15.5	100	125
5^d	$Cp_2Zr(CH_3)_2$ (**III**)	1.5	0	—
6^d	**III** + MAO	1.5	100	394

[a] Polymerization at: temperature, 80°C; pressure, 10 bar; hexane, 70 ml; polymerization time, 1 h; cocatalyst (MAO) was added in the form of solution in toluene.
[b] Total quantity of Zr introduced into the autoclave.
[c] SiO_2–TMCS(325) stands for silica treated with $(CH_3)_3SiCl$ at 325°C.
[d] Polymerization was conducted at 70°C and 6 bar of ethylene pressure in 70 ml of toluene for 1 h.

Table 4
Data on ethylene polymerization [a] with the Cp_2ZrCl_2/SiO_2-TMCS(325)[b] catalyst

Run No.	Cocatalyst	Al:Zr molar ratio	Yield (g PE · (g cat)$^{-1}$)	Activity (kg PE · (mol Zr · h · bar)$^{-1}$)
1	TIBA	150	5.8	176
2	TIBA	1000	4.2	127
3	MAO	100	1.9	55
4	MAO	300	17.8	540
5	MAO	1000	54.5	1638

[a] Polymerization at: temperature, 80°C; pressure, 10 bar; toluene, 70 ml; polymerization time, 1 h; quantity of catalyst, 80–120 mg (Zr content, 0.003 mmol · g^{-1}); cocatalyst was added in the form of solution in hexane (TIBA) or toluene (MAO).
[b] SiO_2–TMCS(325) stands for silica treated with $(CH_3)_3SiCl$ at 325°C.

that they both produce large shapeless aggregates of fine polymer particles. On the contrary, in the absence of MAO, the supported $Cp_2Zr(CH_3)_2/SiO_2$–TMCS catalysts (runs 2–5 in Table 2) give uniform polymer particles 100–300 μm in size. These particles display a spherical shape replicating that of the silica particles. The data obtained suggest that in the absence of MAO the zirconocene is bonded to the surface of silylated silica during a polymerization run, whereas the addition of MAO to the polymerization medium causes the desorbtion of some or all of the metallocene compound from the support and thus the heterogeneous catalytic system acts as a homogeneous one.

We also prepared the metallocene catalyst supported on the completely silylated silica, SiO_2–TMCS(325), using Cp_2ZrCl_2 instead of $Cp_2Zr(CH_3)_2$. The polymerization of ethylene was carried out with this catalyst in combination with TIBA or MAO as cocatalysts. The results are shown in Table 4. The Cp_2ZrCl_2/SiO_2–TMCS(325) catalyst is active in ethylene polymerization with TIBA as the cocatalyst (Table 4, runs 1 and 2). The increase of the TIBA:Zr molar ratio from 150 to 1000 has no marked favorable effect on its activity. When polymerization of ethylene is catalyzed by Cp_2ZrCl_2/SiO_2–TMCS(325) in combination with MAO, the activity of the catalyst is low at Al:Zr ratios ≤ 100, whereas an increase in the Al(MAO):Zr ratio is accompanied by a substantial increase in the catalytic activity up to 1600 kg PE · (mol Zr · h · bar)$^{-1}$ at an Al:Zr ratio =

1000 (Table 4, runs 3–5). However, polyethylene obtained under these conditions consists of shapeless aggregates of polymer particles similar to those usually obtained with homogeneous catalysts. Hence, zirconocene species desorb from the support under action of MAO.

In conclusion, the fact that $Cp_2Zr(CH_3)_2$, when adsorbed on silylated silica, shows a sufficiently high activity in ethylene polymerization, even without any cocatalyst specially added, seems the most intriguing among the results obtained here. We have recently found that the Al^{3+} ions, occurring at the surface of silylated silica as impurities (at ca. 0.04 wt% loading), behave as relatively strong Lewis acids [26]. Presumably, after the removal of Brønsted acid OH groups by silylation, the surface Al^{3+} cations become the main sites which interact with the supported zirconocenes and activate them.

Acknowledgements

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