JOURNAL OF CATALYSIS **121**, 248–261 (1990)

Modification of Olefin Polymerization Catalysts. III. A ^{13}C CP-MAS NMR Study of Adsorption of Silyl Ethers on $MgCl_2$-Supported Ziegler–Natta Catalysts

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Received February 9, 1989

A ^{13}C CP-MAS NMR and elemental analysis study of adsorption and interaction of silyl ethers, $RSi(OMe)_3$ (R = Et, Ph, OMe), as internal and external electron donors with $MgCl_2$-supported Ziegler–Natta catalyst has been carried out. A chemical activation of anhydrous $MgCl_2$ with EtOH and $AlEt_3$ produces a high-surface-area support stabilized by an organoaluminium compound, $AlEt_2(OEt)$. In a treatment of the aluminium-modified $MgCl_2$ support with silyl ether, the aluminium surface complex is retained and silyl ether is almost totally incorporated into the support. ^{13}C CP-MAS NMR data of the methoxy region indicate that a mobile liquid-like silyl ether species dominates, except in the case of $Si(OMe)_4$, where a more strongly bound species is also present on the support. $TiCl_4$ treatment removes the weakly adsorbed silyl ether species, leaving a species which is attributed to an aluminium-bound silyl ether surface complex. No evidence of titanium-bound silyl ether species was found in the solid state or in solution where $TiCl_4$ undergoes with silyl ethers an exchange reaction forming a yellow solid identified as $[TiCl_2(OMe)_2]_x$. Activation of the catalyst with $AlEt_3$ at a high Al : Ti ratio produces a material with a low silyl ether coverage showing a weak methoxy signal in ^{13}C CP-MAS. The linewidths of the observed signals in ^{13}C CP-MAS NMR are in the range 5–10 ppm at every stage of preparation of the catalyst, indicating heterogeneity of the coordination sites on the surface of chemically activated $MgCl_2$.

INTRODUCTION

High activity and stereospecificity are the typical characteristics of the third-generation supported Ziegler–Natta catalysts for α-olefin polymerization (*1–3*). These catalysts comprise a solid catalyst, $MgCl_2/TiCl_4$/electron donor, and a cocatalyst, an aluminium alkyl complexed with an electron donor.

The role of the electron donor, typically an organic Lewis base, in these high-activity catalysts is not very well understood. The electron donor has been suggested to have several functions, such as to complex or to react with $MgCl_2$, $TiCl_4$, and the aluminum alkyl, stabilizing the $MgCl_2$ crystallites, and to inactivate the nonstereospecific polymerization sites thus raising the isotactic index (*4–8*). Recent studies (*9, 10*) show that in the heterogeneous catalyst there are a variety of active sites with different stereospecificity and Lewis acidity. The role of an internal base seems to be in controlling the stereochemistry of the catalyst. The way by which the external base affects the stereospecificity is proposed to be dual, either a poisoning or an activation. The interaction of the free, uncomplexed base with the active sites seems to cause a decrease in isotactic productivity. On the other hand, the base–alkyl metal complex is proposed to be responsible for the activation effect. Evidence for the presence of Lewis base in the environment of the active site has been found (*10*).

Several methods, including polymerization kinetics (*11–14*), elemental analysis (*6*), GC-MS (*5*), EPR (*15*), X-ray analysis (*16*), and IR spectroscopy (*17, 18*) have

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been applied to study Ziegler–Natta-type heterogeneous catalysts. FT-IR spectroscopy has been extensively employed to examine the interaction of electron donors with the support (*17*). More recently, solid-state ^{13}C NMR studies of model compounds related to the Ziegler–Natta catalyst have been presented (*19–21*). High-resolution multinuclear solid-state NMR using magic-angle spinning and dipolar decoupling techniques has also enabled observation of less mobile, strongly adsorbed species on solid supports.

In this paper we describe our ^{13}C CP-MAS NMR results for silyl ethers, $RSi(OMe)_3$ (R = OMe, Et or Ph), adsorbed both as an internal and external electron donor on the Ziegler–Natta-type heterogeneous catalyst, $MgCl_2/ED/TiCl_4/AlEt_3$ or $MgCl_2/ED/TiCl_4/(AlEt_3 + ED)$. Silyl ethers have been found to improve effectively the isotactic productivity in the polymerization of α-olefins by the Ziegler–Natta catalyst (*22–24*). Silyl ethers are also known as internal donors in the patent literature (*25*).

Earlier we presented the results (*26–28*) of our ^{13}C, ^{29}Si NMR, and FT-IR studies on the interaction mechanism in the co-catalyst between the aluminum alkyl and silyl ethers, $Ph_nSi(OMe)_{4-n}$ ($n = 0$–3). $AlEt_3$ and silyl ethers were found in the liquid state to form instantaneously a donor–acceptor complex, which is stable at 1 : 1 molar ratio.

The central purpose of this work is to examine the adsorption of silyl ethers on the support and their possible complex formation with the various constituents of the Ziegler–Natta catalyst.

EXPERIMENTAL

Methods and Materials

Preparation and manipulation of the solid catalysts were all carried out under dry, oxygen-free nitrogen gas (99.998%) using standard inert atmosphere techniques (*29*).

Materials. Solvents, hexane and heptane, were dried over Na and deoxygenated before use. Anhydrous $MgCl_2$ (98%) and $AlEt_3$ (93%) were obtained from Aldrich and used without further purification as was $TiCl_4$ (99.5%) from Riedel-De Haen.

Silyl ethers, $RSi(OMe)_3$ (R = Et, Ph, OMe), were purchased from Petrarch and Aldrich and stored over molecular sieves. Their purity was checked with ^{13}C and ^{29}Si NMR.

NMR spectroscopy. Solution NMR spectra were recorded on a Bruker AM-250 spectrometer operating at 62.9 MHz for ^{13}C-NMR and at 49.7 MHz for ^{29}Si-NMR. The ^{13}C CP-MAS NMR experiments were conducted with the same spectrometer equipped with an auxiliary high-power amplifier and a narrow-bore solid-state probe with magic-angle spinning capability.

The powder samples were placed in a glove bag in two-piece boron nitride/deldrin rotors. The deldrin end caps of the rotor provide a ^{13}C signal at 89 ppm. The magic angle was set by using the ^{79}Br signal of KBr. The Haartman–Hahn matching condition for cross-polarization (CP) was calibrated with adamantane. The ^{13}C CP-MAS spectra were obtained at a spinning speed of 4.7–4.8 kHz using a 14-kHz spectral window with 2.44 Hz data points. The single-contact pulse sequence used a 3-ms contact time (unoptimized). The proton field used for dipolar decoupling during the acquisition time was 10 G. Between 1,000 and 20,000 scans were normally acquired with a 5 s recycle delay. The chemical shifts are reported relative to TMS with use of an external sample of adamantane as reference.

Chemical analysis. The C and H analyses were made using a carbon, hydrogen, nitrogen analyzer CHN-600 (Leco Corporation). Samples were weighed in dry nitrogen atmosphere into small copper samples holders. The samples were burned in an oxygen atmosphere at 950°C, and hydrogen was detected as H_2O using an IR cell and carbon as CO_2 by another IR cell.

Samples for the Mg, Ti, and Al analysis were dissolved in 1 : 1 hydrochloric acid. The metal ions were determined with a Perkin–Elmer 1100 atomic absorption spectrometer. The chlorine content was measured with argentometric titration from the samples dissolved in 7.5 N H_2SO_4. Despite many attempts to determine the silicon content of the samples no satisfactory results could be achieved. The results of the elemental analysis are collected in Table 1.

Surface area determination. The surface areas were determined by the BET method with Accusorb 2200 (Micromeritics) according to the standard ASTM D 3663-78.

Preparation of Catalysts

Activation of $MgCl_2$. Three moles of anhydrous ethanol were added dropwise to a slurry of anhydrous $MgCl_2$ (1 mol) in hexane at ambient temperature. The mixture was stirred for 24 h. The solution was decanted, and the remaining solid was washed with hexane and dried under vacuum. The $MgCl_2 \cdot 3\ EtOH$ thus obtained was treated twice with $AlEt_3$ in hexane to remove the alcohol. The product was separated from the liquid with decantation, washed with hexane, and dried under vacuum. Anal. Found: Mg, 13.3; Cl, 52.4; and Al, 4.7. Characterization of the "active" $MgCl_2$ gave a surface area of 460 m^2/g.

$MgCl_2$/silyl ether. The "active" $MgCl_2$ was stirred for 2 h with an electron donor in hexane at room temperature in a 1:0.5 mole ratio. The product was repeatedly washed with hexane and dried under vacuum.

$MgCl_2$/silyl ether/$TiCl_4$. The product (7 g) obtained in the previous step was reacted with $TiCl_4$ (52 g) in hexane at the reflux temperature for 2 h. The light-brown solid was separated, rinsed with hexane, and dried under vacuum.

$MgCl_2$/silyl ether/$TiCl_4$/$AlEt_3$. The solid from the former step (2.5 g) was treated with $AlEt_3$ in a 1:50 or 1:10 Ti/Al molar ratio in hexane. The mixture was stirred at 50°C for 1 h. The black solid thus obtained was washed with hexane and dried under vacuum.

$MgCl_2$/silyl ether/$TiCl_4$/$AlEt_3$ + silyl ether. The $MgCl_2$/silyl ether/$TiCl_4$ product was stirred in heptane with a heptane solution of $AlEt_3$ and silyl ether in an 1:10 Ti/Al molar ratio for 15 min. The light-brown

TABLE 1

Changes in Chemical Composition at the Stages of Preparation of $MgCl_2$-Supported Catalyst

Material	S_{BET} ($m^2\ g^{-1}$)	Composition (wt%)						Mole ratio of component				
		Mg	Cl	Ti	Al	C	H	Mg	Cl	Ti	Al	ED
$MgCl_2$	460	13.3	52.4	—	4.7	*c*	*c*	1	2.7		0.3	
$MgCl_2/EtSi(OMe)_3$	43	11.9	34.0	—	3.3	19.4	4.7	1	1.96		0.25	0.36[a]
$MgCl_2/EtSi(OMe)_3/TiCl_4$	24	11.3	53.0	8.8	2.7	7.9	2.9	1	3.2	0.40	0.22	0.20[b]
$MgCl_2/EtSi(OMe)_3/TiCl_4/AlEt_3$[d]		12.0	53.0	8.0	1.4	*c*	*c*	1	3.0	0.34	0.11	
$MgCl_2/EtSi(OMe)_3/TiCl_4/(AlEt_3 + EtSi(OMe)_3)$[e]		12.4	52.8	7.7	3.1	9.9	2.1	1	2.9	0.32	0.23	
$MgCl_2/PhSi(OMe)_3$	33	10.8	31.0	—	3.0	27.6	6.5	1	1.97		0.25	0.41[a]
$MgCl_2/PhSi(OMe)_3/TiCl_4$	130	11.6	50.0	5.9	2.9	13.2	2.1	1	3.0	0.26	0.22	0.21[b]
$MgCl_2/PhSi(OMe)_3/TiCl_4/AlEt_3$[d]		13.9	48.0	5.3	4.0	11.8	2.8	1	2.4	0.19	0.26	
$MgCl_2/PhSi(OMe)_3/TiCl_4/(AlEt_3 + PhSi(OMe)_3)$[e]		11.8	47.0	5.4	3.4	18.2	2.8	1	2.7	0.23	0.26	
$MgCl_2/Si(OMe)_4$	95	12.5	34.0	—	3.3	16.7	4.7	1	1.87		0.24	0.32[a]
$MgCl_2/Si(OMe)_4/TiCl_4$	150	10.9	48.0	6.4	*c*	9.2	2.1	1	3.0	0.30		
$MgCl_2/Si(OMe)_4/TiCl_4/AlEt_3$[d]		11.8	44.0	5.6	4.4	*c*	*c*	1	2.6	0.24	0.34	
$MgCl_2/Si(OMe)_4/TiCl_4/AlEt_3$[e]		11.8	43.5	5.6	3.7	11.9	2.9	1	2.5	0.24	0.28	
$MgCl_2/Si(OMe)_4/AlEt_3$		16.3	45.0	—	3.1	12.7	2.6	1	1.9		0.17	

[a] Amount of the electron donor (ED) calculated assuming Al as $Al(OEt)Et_2$.

[b] Amount of the electron donor (ED) calculated assuming Al as $Al(OEt)Cl_2$.

[c] Not determined.

[d] Ti:Al = 1:50 in the activation.

[e] Ti:Al = 1:10 in the activation.

solid was separated, washed repeatedly with heptane, and dried under vacuum.

Reaction of silyl ether with $TiCl_4$. Silyl ether was reacted with $TiCl_4$ in a 0.9 : 1 molar ratio in hexane. The reaction mixture was stirred for 2 h at room temperature. A yellow solid separated from the reaction mixture. It was isolated, washed with hexane, and dried under vacuum. The solid was identified as $[TiCl_2(OCH_3)_2]_x$ on the basis of the elemental analysis. Anal. Calcd. for $[TiCl_2(OCH_3)_2]_x$: Ti, 26.5; Cl, 39.2; C, 13.3; H, 3.3. Anal. Found: Ti, 24; Cl, 39; C, 12.2; H, 2.9. ^{13}C CP-MAS NMR 72.2(s), 76.7(s) ppm.

RESULTS AND DISCUSSION

The $MgCl_2$-supported Ziegler–Natta catalysts were prepared according to Scheme I. Adsorption of silyl ethers, $RSi(OMe)_3$ (R = Et, Ph, OMe), on the catalyst was studied with ^{13}C CP-MAS and elemental analysis. The steps in Scheme I are discussed in detail.

Activation of $MgCl_2$

The chemical activation of $MgCl_2$ was performed by treating anhydrous $MgCl_2$ with an activating agent, ethanol. The "active" $MgCl_2$ was obtained by a reaction of $MgCl_2 \cdot 3EtOH$ with $AlEt_3$. It contains according to the chemical analysis 4.7 wt% of aluminium (Table 1.). In the ^{13}C CP-MAS spectrum (Fig. 1) of the "active" $MgCl_2$ there are three major signals at 60.0, 17.9, and 7.3 ppm, which can be assigned to $[AlEt_2(OEt)]_2$ on the basis of the chemical shift data. In heptane solution, $[AlEt_2(OEt)]_2$ shows resonances at 59.34, 18.45, 8.79, and ~0 ppm (*30*). $[AlEt_2(OEt)]_2$ is formed in the reaction of $AlEt_3$ with EtOH (*31*).

Adsorption of $[AlEt_2(OEt)]_2$ on $MgCl_2$ is possible either through coordination of the ethoxy oxygen to Mg^{2+} (Scheme II) or through chloride bridges (Scheme III). The former type of coordination is feasible since magnesium halides are known to form numerous crystalline solvates such as $MgX_2 \cdot$

$$(1)\quad MgCl_2 + 3\,EtOH \xrightarrow[25^\circ C,\ 24\ h]{hexane} MgCl_2 \cdot 3EtOH$$

$$(2)\quad MgCl_2 \cdot 3EtOH + 3\,AlEt_3 \xrightarrow[25^\circ C,\ 24h]{hexane} \text{"}MgCl_2\text{"}$$

$$(3)\quad \text{"}MgCl_2\text{"} + 0.5\,ED \xrightarrow[25^\circ C,\ 2h]{hexane} MgCl_2/0.5\,ED$$

$$(4)\quad MgCl_2/0.5\,ED + 8.5\,TiCl_4 \xrightarrow[reflux,\ 2.5\ h]{hexane} MgCl_2/ED/TiCl_4$$

$$(5)\quad MgCl_2/ED/TiCl_4 + 50\,AlEt_3 \xrightarrow[50^\circ C,\ 1h]{hexane} MgCl_2/ED/TiCl_4/AlEt_3$$

$$(6)\quad MgCl_2/ED/TiCl_4 + 10\,AlEt_3 * ED \xrightarrow[25^\circ C,\ 15\ min]{heptane} MgCl_2/ED/TiCl_4/AlEt_3{*}ED$$

SCHEME I. Activation of anhydrous $MgCl_2$ (1–2) and preparation of a $MgCl_2$-supported catalyst (3–6).

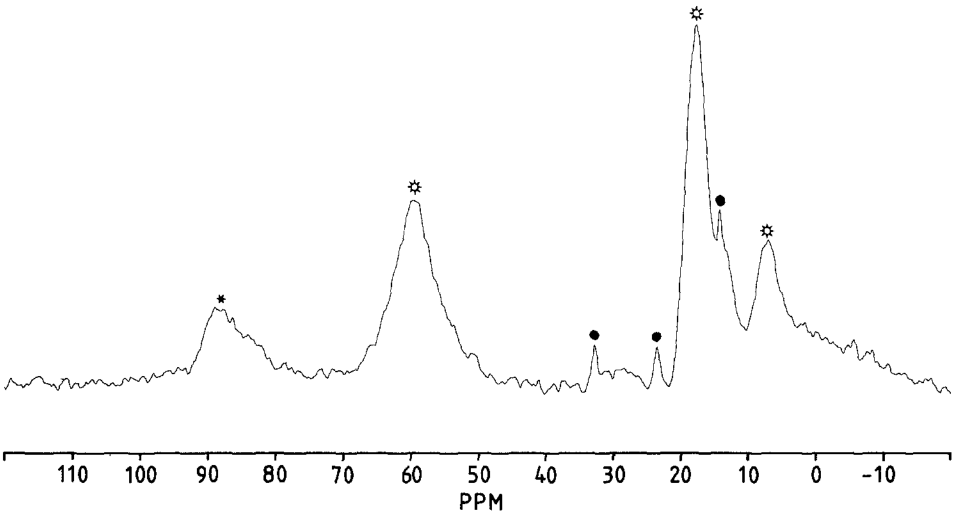
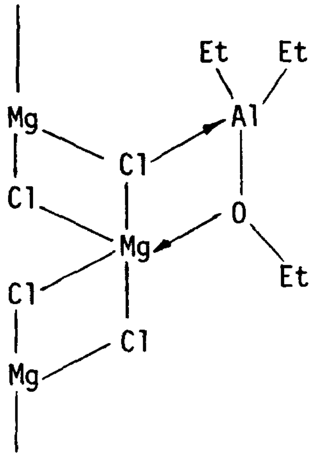


FIG. 1. ^{13}C CP-MAS spectrum of the "active" $MgCl_2$. ^{13}C signals of delrin (*), hexane (●), and $AlEt_2OEt$ (☼).

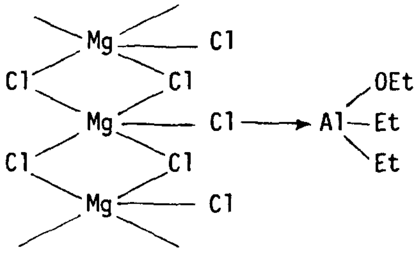
6 ROH and $MgX_2 \cdot 3\ Et_2O$ (*32*). Moreover, alkoxy bridges between aluminium and magnesium have been observed in solid state in $Mg[Al(CH_3)_2(OMe)_2]_2 \cdot C_4H_8O_2$ (*33*) and in Mg(9,10-dihydro-9,10-anthrylene) $AlEt_2(OEt)(THF)_3$ (*34*). The complexation type shown in Scheme III has been previously proposed by Chien *et al.* (*6*) for $MgCl_2$ and $EtAl(OR)_2$ (R = *p*-methylphenoxy).

In addition, the relatively large upfield shifts (~5 and 1.5 ppm in Table 2) of the CH_2Al and CH_3CH_2Al resonances imply a change in shielding of the aluminium-bound carbon atoms. This can be interpreted by a coordination of chloride to aluminium (in Scheme II) or a complex formation by a chloride bridge (Scheme III). The coordination of internal donor has been reported to be more likely on the (110) face of $MgCl_2$ crystals than on the (100) face, since the (110) face is more Lewis acidic (*35*).

The complexes formed according to Schemes II or III are rather firmly retained on the $MgCl_2$ support, since a further treatment of the "active" $MgCl_2$ with $AlEt_3$ or washing with hexane does not remove the surface organoaluminium compound. Moreover, as can be seen later, a treatment



SCHEME II. Proposed coordination of $AlEt_2OEt$ on the (110) face of $MgCl_2$. (The entire coordination sphere of Mg^{2+} is not shown.)



SCHEME III. Proposed coordination of $AlEt_2OEt$ on the (100) face of $MgCl_2$.

TABLE 2

^{13}C Chemical Shifts (in ppm from $Si(Me)_4$) for Ethanol, Sorbed Ethanol, and Ethoxy Group

	OCH_2	OCH_2CH_3	$AlCH_2CH_3$	$AlCH_2$
EtOH[a]	57.3	17.9		
$MgCl_2$/EtOH[b]	59.5	18.54, 17.80		
$(AlEt_2OEt)_2$[a]	59.34	18.45	8.79	0
$MgCl_2/AlEt_2OEt$[b]	59.96	17.93	7.28	−5

[a] Ref. (*30*).

[b] This work.

of $MgCl_2$ even with an electron donor or $TiCl_4$ does not remove all aluminium.

The aluminium-modified "active" $MgCl_2$ has a high surface area of 460 m^2/g. The aluminium compound on the modified $MgCl_2$ ($MgCl_2 \cdot 0.3AlEt_2(OEt)$) can be regarded as a surface complex. The broad ^{13}C resonances of $AlEt_2(OEt)$ in the CP-MAS spectrum are typical for a heterogeneous material. Heterogeneity of the coordination sites on the $MgCl_2$ surface will lead to a distribution of chemical shifts of the $AlEt_2(OEt)$ resonances and appear as a line broadening. In a calculation of the surface area covered by the aluminium compound a coordination type shown in Scheme II was assumed. Van der Waals areas of 23–42 Å^2 were estimated for the adsorbed $AlEt_2(OEt)$, depending on the bonding angles around Al and oxygen of the methoxy group. A surface coverage of 50–90% monolayer was calculated for the activated $MgCl_2$.

Thus the function of the organoaluminium compound in the support can be considered to be to stabilize the $MgCl_2$ crystallites fractured in the chemical activation and to prevent their agglomeration.

$MgCl_2/RSi(OMe)_3$

The incorporation of $RSi(OMe)_3$ as an internal electron donor into the "active" $MgCl_2$ support was performed in a $MgCl_2$: ED ratio of 1 : 0.5. The relatively high electron donor content ($ED/MgCl_2$ = 0.32–0.41, Table 1) of the $MgCl_2$ solid obtained indicates almost a quantitative incorporation of the electron donor into $MgCl_2$. Introduction of electron donor into $MgCl_2$ is also associated with a decrease in the specific surface area of the support. A surface area of 33–95 m^2/g was measured for $MgCl_2/RSi(OMe)_3$ (see Table 1).

The treatment of the $MgCl_2$ support with the silyl ethers does not remove the organoaluminium compound on the basis of NMR results. The results of the aluminium analysis, which were of the order 3–3.3 wt% for the all three $MgCl_2/RSi(OMe)_3$ (R = Et, Ph, OMe) materials, also support this result.

The ^{13}C CP/MAS spectra of the high-surface-loading silyl ether on $MgCl_2$ are presented in Figs. 2–4. In addition to the signals of the $MgCl_2$-attached organoaluminium compound, the spectra of the methoxy region are dominated by a single broad resonance at 50–51 ppm due to the silicon-bound methoxy carbon. In the case of $Si(OMe)_4$ there is another lower shielding resonance at 56 ppm.

The major resonance at 50.7–51.5 ppm is only slightly shifted from the ^{13}C isotropic chemical shift of liquid silyl ethers at 50.2–50.9 ppm (Table 3). Thus most of the silyl ethers, $RSi(OMe)_3$ (R = Et, Ph, OMe), held on the $MgCl_2$ support at this loading level can be considered as "intercrystalline fluid" (*36*) which does not experience a strong interaction with the support. The lower surface area of the supports is also an

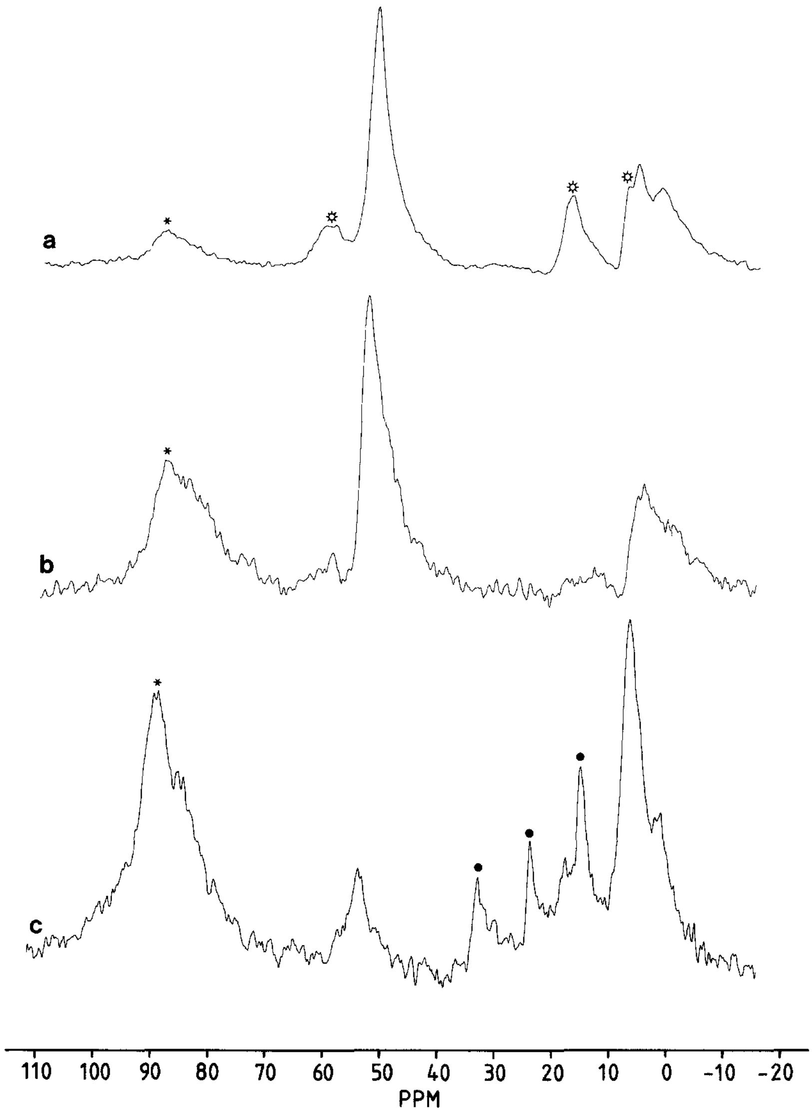


FIG. 2. ^{13}C CP-MAS spectra of $EtSi(OMe)_3$. (a) $MgCl_2$/ED, (b) $MgCl_2$/ED/$TiCl_4$, (c) $MgCl_2$/ED/$TiCl_4$/$AlEt_3$ (Ti : Al = 1 : 50). ^{13}C signals of delrin (*), hexane (●), and $AlEt_2OEt$ (☼).

indication of a liquid-like electron donor coverage.

The down-field resonance at 56 ppm of the $MgCl_2/Si(OMe)_4$ material could be due to magnetic inequivalence in the carbon atoms of the four methoxy groups or due to another methoxy site which is immobilized by a stronger interaction with the support. The results from the corresponding ^{13}C CP-MAS NMR spectra of the other silyl ethers, $RSi(OMe)_3$ (R = Et, Ph), do not seem to support the former assumption.

For $MgCl_2/Si(OMe)_4$ with 0.40 g of $Si(OMe)_4$/1 g of $MgCl_2$, a 1.5-monolayer coverage has been estimated. In the surface area calculation, a model, in which Si $(OMe)_4$ is attached to the activated $MgCl_2$ surface at its oxygen of one methoxy group and the rest of the molecule has an average van der Waals area of 44 Å^2, was assumed.

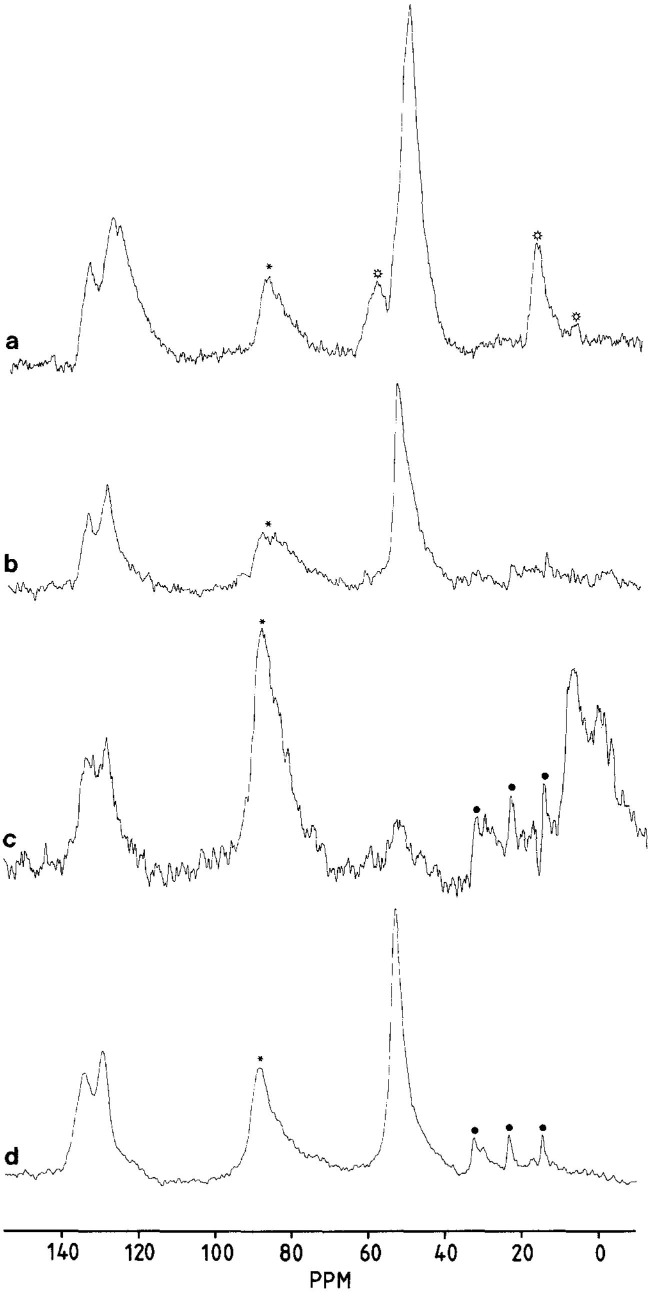


FIG. 3. ${}^{13}C$ CP-MAS spectra of $PhSi(OMe)_3$. (a) $MgCl_2/ED$, (b) $MgCl_2/ED/TiCl_4$, (c) $MgCl_2/ED/TiCl_4/AlEt_3$ (Ti : Al = 1 : 50), (d) $MgCl_2/ED/TiCl_4/AlEt_3$ * ED. ${}^{13}C$ signals of delrin (*), hexane or heptane (●), and $AlEt_2OEt$ (☼).

$MgCl_2/RSi(OMe)_3/TiCl_4$

The $TiCl_4$ treatment of the $MgCl_2/ED$ material resulted in the Ti/Mg ratio of 0.26 : 1–0.40 : 1. The highest loading of the support was achieved in the case of $MgCl_2/EtSi(OMe)_3$. This can be reflecting a smaller steric hindrance of the ethyl group compared to that of the phenyl or methoxy group.

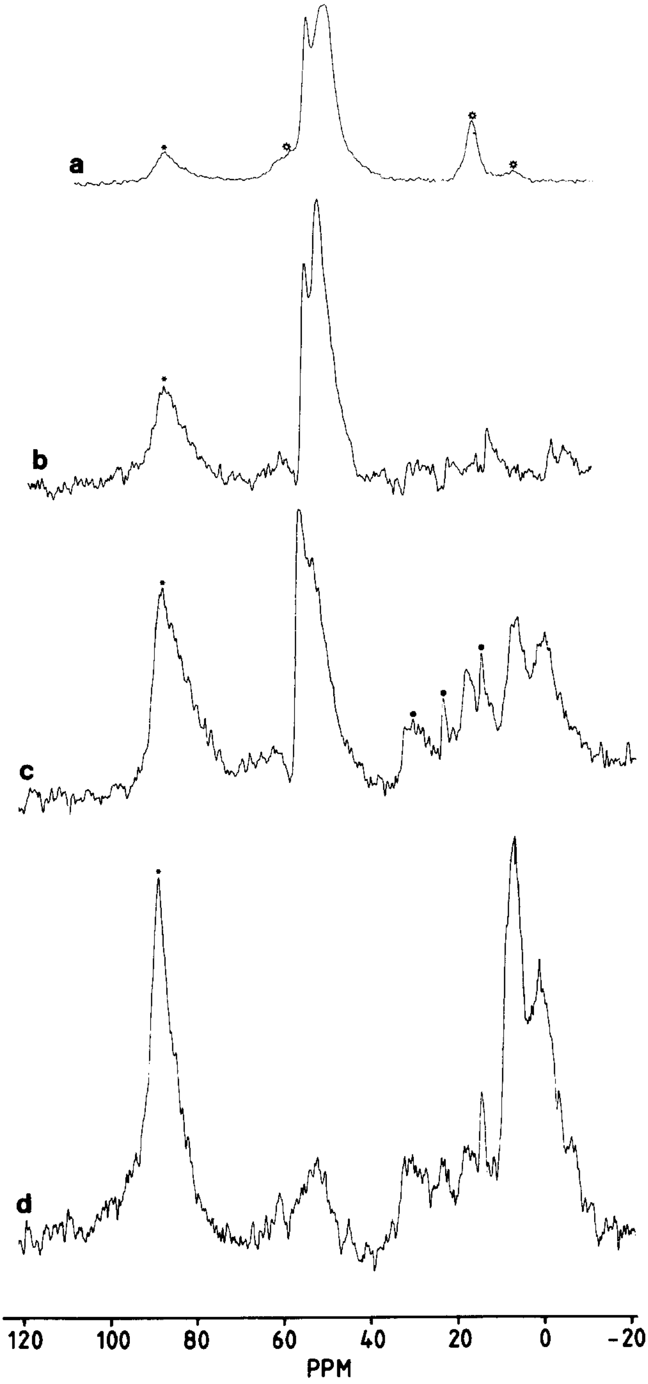


FIG. 4. ^{13}C CP-MAS spectra of $Si(OMe)_4$. (a) $MgCl_2/ED$, (b) $MgCl_2/ED/TiCl_4$, (c) $MgCl_2/ED/TiCl_4/AlEt_3$ (Ti : Al = 1 : 10), (d) $MgCl_2/ED/TiCl_4/AlEt_3$ (Ti : Al = 1 : 50). ^{13}C signals of delrin (*), hexane (●), and $AlEt_2OEt$ (✡).

TABLE 3

^{13}C Chemical Shifts (in ppm from $Si(Me)_4$) of the ^{13}C Resonance of the OCH_3 Group of the Electron Donor (ED) at the Stages of the Preparation of $MgCl_2$-Supported Catalysts

Material	ED		
	$EtSi(OMe)_3$	$PhSi(OMe)_3$	$Si(OMe)_4$
$MgCl_2$/ED	51.4	50.7	51.5, 56.0
$MgCl_2$/ED/$TiCl_4$	53.3	53.4	53.1, 56.2
$MgCl_2$/ED/$TiCl_4$/$AlEt_3$[a]	53.8	53.2	52.4
$MgCl_2$/ED/$TiCl_4$/$AlEt_3$[b]			53.0, 56.4
$MgCl_2$/ED/$TiCl_4$/$AlEt_3$ * ED[b]	[c]	53.0	
$MgCl_2$/ED/$AlEt_3$		53.9	
ED in C_6D_6[d]	50.2	50.6	50.9
ED * $AlEt_3$ in C_6D_6[d]	53.5	53.6	53.7

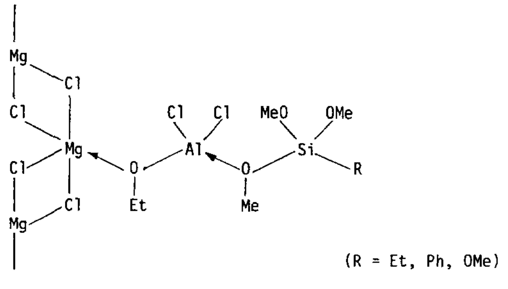
[a] Ti : Al = 1 : 50 in the activation.
[b] Ti : Al = 1 : 10 in the activation.
[c] Not measured.
[d] Ref. (*27*).

Incorporation of titanium into $MgCl_2$ is associated with displacement of almost half of the electron donor content (Table 1). Similar removals of electron donors, e.g., *p*-cresol (*6*), 1-butanol (*4*), and ethyl benzoate (*7, 8, 17*) from a $MgCl_2$ support by the $TiCl_4$ treatment have been previously observed. The reaction with $TiCl_4$ also removes some of the aluminium incorporated into $MgCl_2$. After the $TiCl_4$ treatment the Al : ED molar ratio in the $MgCl_2$/ED/$TiCl_4$ (ED = $EtSi(OMe)_3$ and $PhSi(OMe)_3$) is close to 1 : 1. In the cases of $PhSi(OMe)_3$ and $Si(OMe)_4$ the surface areas of the solids obtained have increased to 130 and 150 m^2 g^{-1}, respectively.

The ^{13}C CP-MAS spectra of the $MgCl_2$/ED/$TiCl_4$ materials (Figs. 2–4) clearly suggest that the ethyl substituents of aluminium have been replaced by chlorines, since the ^{13}C signals due to the aluminium-bound CH_2CH_3 are no longer visible. The chlorination of $AlEt_3$ by $TiCl_4$ is well known (*6*). The ^{13}C signals of the aluminium-bound OCH_2CH_3 group are poorly observable. The low intensity may be due to a poor cross-polarization efficiency which probably results from a weak ^{13}C–^{1}H dipolar coupling due to changes in mobility after removal of the excess electron donor and due to the chlorination of aluminium. The methoxy resonances of the three electron donors in the ^{13}C CP-MAS spectra have shifted ca. 2 ppm downfield upon $TiCl_4$ treatment. In addition to the resonance at 53.1 ppm the spectrum of $MgCl_2$/$Si(OMe)_4$/$TiCl_4$ contains also the lower-shielding signal at 56.2 ppm.

The electron donors do not seem to be directly bound or complexed to titanium, since the ^{13}C resonances due to the methoxy groups of the silyl ethers are only slightly shifted after the $TiCl_4$ treatment. The titanium-bound OCH_2 species are known (*38*) to resonate at 66–76 ppm and the titanium-bound OCH_3 species at 72–76 ppm in ^{13}C CP-MAS NMR. Detection of possible titanium complexed or bound silyl ether species is hampered somewhat by the broad ^{13}C resonance of delrin at 89 ppm. However, from the CP-MAS spectrum of $MgCl_2$/$PhSi(OMe)_3$/$TiCl_4$ it is clear that the major amount of silyl ethers is not directly bound or complexed to titanium, on the basis on the intensity ratio of the carbon resonances of the methoxy and phenyl groups. In addition, in solution silyl ethers do not form stable isolatable complexes with $TiCl_4$ as do esters or ketones (*41*), but undergo with $TiCl_4$ an exchange reaction of chlorides and methoxy groups (*39*). Thus, in the reactions of $RSi(OMe)_3$ (R = OMe, Et, Ph) with $TiCl_4$ the isolated product was a yellow solid which was identified as $[TiCl_2(OMe)_2]_x$ on the basis of elemental analysis. Its ^{13}C CP-MAS spectrum shows two signals at 72.2 and 76.7 ppm. This splitting of the titanium-bound methoxy signals can be due to a polymeric structure with bridging and terminal methoxy groups (*38*).

The chemical shifts of the resonances at 53 ppm of the $MgCl_2/RSi(OMe)_3/TiCl_4$ catalysts are equal to those of the methoxy resonances of the $AlEt_3 * RSi(OMe)_3$ complexes found in solution state (Table 3). Thus the resonances at 53 ppm could correspond to $Al * RSi(OMe)_3$-type species (Scheme IV). A single ^{13}C signal is observed for the complexed and uncomplexed, magnetically inequivalent methoxy carbons. The breadth of the OCH_3 resonance can reflect a distribution of isotropic chemical shifts for the complexed and uncomplexed methoxy groups of $RSi(OMe)_3$ attached to the heterogeneous modified surface. A molecular motion of the methoxy groups accompanied by a chemical exchange process interconverting them could be another phenomenon contributing to the broadening of the OCH_3 signal. In fact, in solution the averaging of the methoxy carbon signals of $RSi(OMe)_3$ upon complexation with $AlEt_3$ is observed (*27*). The Al/ED mole ratio of 1.1 found in $MgCl_2/EtSi(OMe)_3/TiCl_4$ and $MgCl_2/PhSi(OMe)_3/TiCl_4$ also supports a 1 : 1-type coordination between Al and the electron donor.



SCHEME IV. Proposed coordination of the electron donor to the modified $MgCl_2$ surface.

In addition, a treatment of $MgCl_2/Si(OMe)_4$ with $AlEt_3$ affords a material, the ^{13}C CP-MAS spectrum of which (Fig. 5) shows in the methoxy region a broad resonance at 53.9 ppm, in accordance with the Al–silyl ether coordination model.

If the most probable coordination sites for the proposed silyl ether–aluminium complex are the more acidic (110) crystal faces of $MgCl_2$, then $TiCl_4$ can most easily bind to the more basic (100) faces (*8*).

The downfield resonance of $Si(OMe)_4$ at 56 ppm can correspond to a coordination site in which $Si(OMe)_4$ is bound directly to the $MgCl_2$ support. This is supported by an observed ^{13}C CP-MAS spectrum of a nonactivated $MgCl_2/Si(OMe)_4$ material, which contains two methoxy signals in an intensity ratio of 2 : 3 at 52.9 and 56.7 ppm, respectively.

$MgCl_2/RSi(OMe)_3/TiCl_4/AlEt_3$

Alkylation of Ti and reduction of Ti^{4+} to Ti^{2+} or Ti^{3+} has been reported (*6*) to be the major effects of the activation of the $MgCl_2/ED/TiCl_4$ catalyst with $AlEt_3$.

The elemental analysis (Table 1) performed after the $AlEt_3$ treatment of $MgCl_2/RSi(OMe)_3/TiCl_4$ (in a Ti/Al mole ratio of 1 : 50 or in the case of $Si(OMe)_4$ also in a Ti/Al ratio of 1 : 10) reveals a decrement in the chlorine and titanium content and a slight increase in the aluminium content. The amount of silyl ethers in the support after the $AlEt_3$ treatment is difficult to estimate only on the basis of the CH analysis because of the various oxidation states of Ti (+4, +3, or +2) and the ambiguous content of chlorination of Al.

The ^{13}C CP-MAS spectra (Figs. 2–4) of the $AlEt_3$-treated materials (in a Ti/Al mole ratio of 1 : 50) contain unexpectedly a

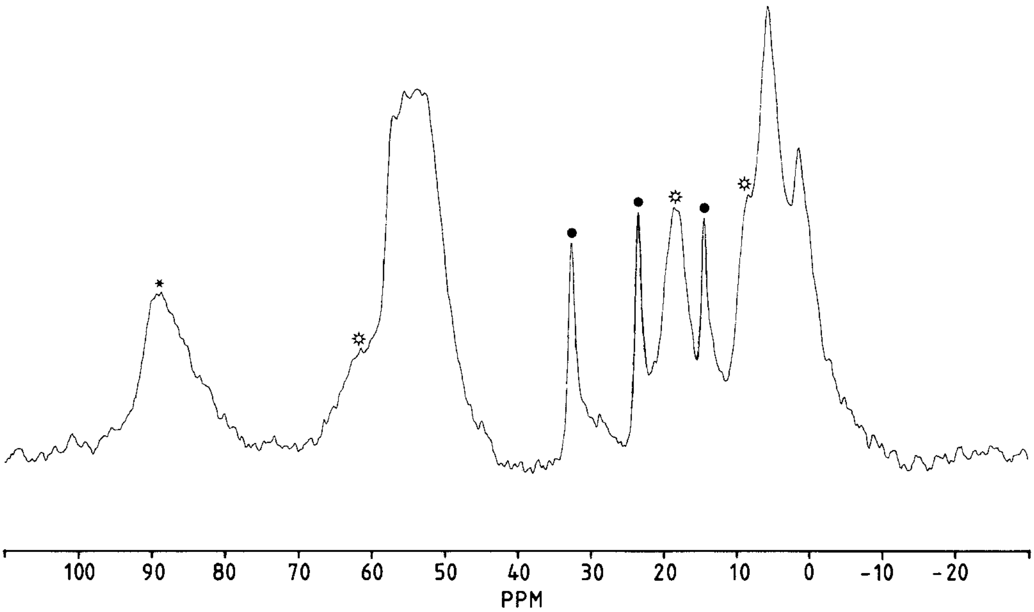


FIG. 5. ^{13}C CP-MAS spectrum of $MgCl_2/Si(OMe)_4/AlEt_3$. ^{13}C signals of delrin (*), hexane (●), and $AlEt_2OEt$ (☼).

methoxy signal at 52.4–53.8 ppm of very low intensity if for example one considers the intensity of the methoxy signal relative to that of the phenyl resonance in the spectrum of $MgCl_2/PhSi(OMe)_3/TiCl_4/AlEt_3$. In the case of $PhSi(OMe)_3$ the methoxy signal at 53.2 ppm contains also a spinning sideband of the aromatic carbon resonance due to chemical shift anisotropy.

The chemical shifts of the methoxy resonances of $RSi(OMe)_3$ are nearly equal to those of the aluminium-complexed silyl ethers in solution. Thus one can conclude that most of the silyl ethers are still complexed to the aluminium sites of the support. The low intensity of the methoxy resonances of the electron donors may arise from several factors. A gradual alkylation of the silyl ethers by $AlEt_3$ can occur under the conditions (at 50°C in the presence of a large excess of $AlEt_3$ (Al : ED ~ 50 : 1)) in which the $AlEt_3$ treatment of $MgCl_2/ED/TiCl_4$ was carried out. These conditions enhance the ether reduction and formation of alkylated silyl ethers (*27*). At least some of the electron donor in $MgCl_2/ED/TiCl_4/AlEt_3$ may be in the alkylated form $RSi(Et)_x(OMe)_{3-x}$. The detection of the ethyl resonances of the alkylated silyl ethers at 4–7 ppm (*27*) is obscured by the ethyl signals of $AlEt_3$ resonating at the same field. The loss of intensity in the methoxy resonance can also be due to a poor cross-polarization efficiency as observed earlier for the OCH_2CH_3 resonances of the aluminium compound.

The methoxy signal at 56 ppm is not visible any longer in the ^{13}C CP-MAS spectrum of $MgCl_2/Si(OMe)_4/TiCl_4/AlEt_3$. On the other hand, after the $AlEt_3$ treatment of $MgCl_2/Si(OMe)_4/TiCl_4$ in a Ti : Al ratio of 1 : 10 the resonance at 56 ppm is observed with a poorly resolved resonance at 53 ppm of lower intensity, probably due to a higher silyl ether content. The ratio of Al to Ti in the 1 : 10 and 1 : 50 activated catalysts does not, however, differ much, ranging from 1.1 : 1 to 1.4 : 1.

The presence of paramagnetic Ti^{3+} species on the support after $AlEt_3$ activation of the catalyst cannot be deduced from the ^{13}C CP-MAS spectra. Nineteen percent of the

Ti^{3+} species in the catalyst have been observed (*6*) by EPR to be paramagnetic. The remaining Ti^{3+} is EPR-inactive and probably dimeric. If the adsorption site is paramagnetic, the NMR lines of the molecules interacting with this site are normally broad and weak (*40*). A direct interaction of silyl ether with the paramagnetic Ti^{3+} site can be excluded on the basis of undetected line broadening after the $AlEt_3$ treatment. In addition, no direct complexation of silyl ethers to Ti species was observed at the previous stage.

$MgCl_2/ED/TiCl_4/AlEt_3 * ED$

Activation of the titanium catalyst with a mixture of $AlEt_3$ and external electron donor has been reported to produce less divalent titanium sites than activation with $AlEt_3$ (*6*).

Activation of the $MgCl_2/RSi(OMe)_3/TiCl_4$ (R = Et, Ph) catalyst with a hexane solution of $AlEt_3$ and electron donor, $RSi(OMe)_3$ (R = Et, Ph), was performed in a 1 : 1 mole ratio, in which concentration $AlEt_3$ and silyl ethers form a stable complex, $AlEt_3 * ED$, and do not undergo a rearrangement reaction (*27*). This type of activation produces a material with almost the same composition as that obtained after a plain $AlEt_3$ treatment. The Al : Ti ratio is lower (1.1) than the corresponding value (1.4) obtained in the $AlEt_3$ activation since a 1 : 10 Ti : Al ratio was used in the $AlEt_3 *$ ED activation.

The ^{13}C CP-MAS spectrum of $MgCl_2/PhSi(OMe)_3/TiCl_4/AlEt_3 * PhSi(OMe)_3$ shows a single methoxy resonance at 53 ppm of higher intensity than that observed in $MgCl_2/PhSi(OMe)_3/TiCl_4/AlEt_3$. Probably a higher silyl ether content of the support can be one of the factors leading to a more intense methoxy signal for $PhSi(OMe)_3$. This result is supported by similar observations made for $Si(OMe)_4$ after the $AlEt_3$ activation with an 1 : 10 Ti : Al ratio.

The chemical shift of the methoxy resonance at 53 ppm in the ^{13}C spectrum of $MgCl_2/PhSi(OMe)_3/TiCl_4/AlEt_3 * PhSi(OMe)_3$ corresponds to the chemical shift of $PhSi(OMe)_3$ complexed to aluminium, as earlier observed. However, in this case there are no aluminium-bound ethyl resonances visible in the spectrum.

As a result of the $AlEt_3$ and $AlEt_3 *$ ED activations, the Al : Ti ratio of the activated catalyst seems to be determined by the Ti : Al ratio used in the activation regardless of the activation type. As observed for $Si(OMe)_4$ and $PhSi(OMe)_3$ the activation with a 1 : 10 Ti : Al ratio produces a material with Al : Ti ratio of 1.1 whereas the activation with a 1 : 50 ratio affords for the catalyst a 1.4 Al : Ti ratio.

CONCLUSIONS

It is evident from the present results that ^{13}C NMR spectroscopy in conjunction with CP-MAS methods can be used to probe the interaction between an electron donor and Ziegler–Natta catalyst at natural ^{13}C isotope abundance if a high enough loading level of adsorbate is used.

The structure and exact assignment of the coordination site of silyl ethers on the $MgCl_2$ support is not unambiguous on the basis of mere ^{13}C CP-MAS NMR, where relatively small changes in the isotropic chemical shift were found for the methoxy group of the silyl ether species on adsorption. A small change in the isotropic chemical shift does not necessarily reflect the real changes in the electronic environment of the methoxy group of $RSi(OMe)_3$ upon coordination, since the large opposing changes in the three components of the chemical shift tensor can cancel and result in a small change in the isotropic chemical shift as observed for $[MgCl_2TiCl_4(MeCO_2Et)_4]$ (*21*).

^{29}Si and ^{27}Al CP-MAS NMR could give more information for identification of surface-bonding sites on the basis of larger nuclear shielding range of these nuclei. Nevertheless, the ^{13}C spectral evidence suggests that silyl ethers as internal electron donors do not coordinate to titanium sites. Thus, silyl ethers as internal donors can direct coordination of $TiCl_4$ on the $MgCl_2$ crystal faces but cannot control stereospecificity of the active Ti sites. Silyl ethers forming rather stable complexes with $AlEt_3$ have an important use as external electron donors.

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