

## $^{27}\text{Al}$ NMR MAS study of $\text{AlEt}_{3-n}\text{Cl}_n/\text{MgCl}_2$ systems

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### Abstract

The  $^{27}\text{Al}$  NMR MAS spectra of surface species of aluminum-containing compounds  $\text{AlEt}_{3-n}\text{Cl}_n$  ( $n = 0-3$ ) on  $\text{MgCl}_2$  have been measured. The data obtained indicate that 5- and 6-coordinated aluminum compounds form on the  $\text{MgCl}_2$  surface. The majority of the  $\text{AlCl}_3$  supported in small amounts on  $\text{MgCl}_2$  was found to be 4-coordinated. © 1997 Published by Elsevier Science B.V.

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### 1. Introduction

Organoaluminum compounds (OAC) are important co-catalysts of both conventional Ziegler–Natta catalysts and of highly active supported catalysts for olefin polymerization with a composition of  $\text{TiCl}_4/\text{MgCl}_2$ . As OAC interacts with the supported catalyst, it alkylates and reduces titanium chloride. Besides, the initial OAC and the products of its reaction with  $\text{TiCl}_4$  adsorb tightly on the catalyst (Ti and Mg chlorides) [1]. Compound  $\text{AlEt}_{3-n}\text{Cl}_n$  ( $n = 0-3$ ) and  $\text{TiCl}_4$  are both Lewis acids. So, OAC and  $\text{TiCl}_4$  are likely to react with the same centers on the surface of highly dispersed  $\text{MgCl}_2$ . Therefore, the knowledge on the state and structure of OAC adsorbed on  $\text{MgCl}_2$  can help to understand the composition of the active component of the catalyst as well as the polymerization mechanism.

In recent years high-resolution solid state NMR spectroscopy is widely used to study supports and catalysts [2–4].  $^{27}\text{Al}$  NMR is a very promising tool to study the state of Al sites. It has been shown for aluminum oxides, zeolites and aluminosilicates [5], that the position of the  $^{27}\text{Al}$  NMR MAS line depends on the Al coordination. When oxygen is surrounding, a chemical shift of 0–10 ppm corresponds to octahedral coordination of Al, that of 25–35 ppm to pentahedral, and 60–100 to tetrahedral coordination.

$^{27}\text{Al}$  NMR is well recognized as a method to study OAC-containing solutions. In [6] the NMR spectral parameters have been determined for a number of compounds  $(\text{R}_{3-n}\text{AlX}_n)_m$  ( $n = 0-3$ ,  $m = 1-3$ , X = H, Cl, OR). The  $^{27}\text{Al}$  NMR chemical shifts were shown to correlate with the Al coordination number. For the 3-coordinated Al in  $\text{R}_3\text{Al}$  monomers, chemical shifts range from 280 to 210 ppm; for the 4-coordinated Al in complexes  $(\text{R}_{3-n}\text{AlX}_n)_m$  ( $n = 0-2$ ,  $m = 2-3$ ) chemical shifts range from 180 to 125 ppm, and for the 5-coordinated Al from 120 to 100

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ppm. The chemical shift of 4-coordinated Al in inorganic compounds differs from that in organic ones since the aluminum–carbon bond in the latter causes the line to shift to lower fields (i.e., the chemical shift increases). In practice, the typical chemical shifts of 4-coordinated Al inorganic and 5-coordinated Al organic compounds overlap.

In this work we have used  $^{27}\text{Al}$  NMR MAS to study OAC with composition  $\text{AlEt}_{3-n}\text{Cl}_n$  ( $n = 0–3$ ) supported on a highly dispersed  $\text{MgCl}_2$ . Based on the data obtained, we will discuss the coordination state of Al atoms and the structure of the adsorbed complexes.

## 2. Experimental

As a support we used highly dispersed  $\text{MgCl}_2$  (BET surface area  $82 \text{ m}^2/\text{g}$ ) prepared by the interaction of Mg and BuCl according to the procedure described in [7]. Hexane solutions of  $\text{AlEt}_3$ ,  $\text{AlEt}_2\text{Cl}$ ,  $\text{AlEtCl}_2$  and a toluene solution of  $\text{AlCl}_3$  were used for the support as follows.  $\text{MgCl}_2$  and hexane were loaded into the glass reactor under Ar atmosphere, then a solution of OAC was added at a molar ratio  $\text{Al}/\text{Mg} \approx 1$  under stirring and kept with  $\text{MgCl}_2$  at ambient temperature for 40–60 min. The resulting product was washed with hexane and dried in vacuum. The Al content in the samples obtained was as follows (in wt%): 0.65 ( $\text{AlEt}_3/\text{MgCl}_2$ ), 0.68 ( $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ ), 0.70 ( $\text{AlEtCl}_2/\text{MgCl}_2$ ). Two  $\text{AlCl}_3/\text{MgCl}_2$  samples were prepared by mixing the  $\text{AlCl}_3$  solution with  $\text{MgCl}_2$  in toluene under the following conditions: (1) molar ratio  $\text{Al}/\text{Mg} = 0.25$ ,  $80^\circ\text{C}$  (3.6 wt% of Al in the sample); (2) molar ratio  $\text{Al}/\text{Mg} = 0.01$ , ambient temperature, a slow 30 min dosing of  $\text{AlCl}_3$  solution into the reactor (0.31 wt% of Al in the sample).

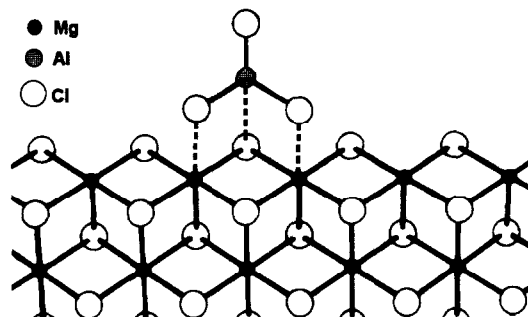
The amount of OAC supported via saturation (0.65–0.7 wt% or  $\sim 0.25 \text{ mmol Al/g}$ ) corresponds to the number of Lewis acid centers on the  $\text{MgCl}_2$  surface ( $0.17 \text{ mmol/g}$ ) and to the

amount of  $\text{TiCl}_4$  supported on similar  $\text{MgCl}_2$  at ambient temperature ( $0.23 \text{ mmol/g}$ ) [8].

The  $^{27}\text{Al}$  NMR spectra were recorded using a Bruker MSL-400 spectrometer ( $^{27}\text{Al}$  resonance frequency of 104.3 MHz) in the frequency range of 100 kHz, with a pulse width of  $2 \mu\text{s}$  ( $\pi/12$ ) and 0.2 s delay between pulses. Magic angle spinning in the Andrew-Beams PMMA rotors (rotation frequency ca. 4 kHz) was applied. Chemical shifts were referenced to the external 1 M aqueous solution of  $\text{AlCl}_3$ . In order to avoid contact of the sample with air, weighed portions (0.1–0.2 g) were loaded into the NMR rotor under Ar atmosphere and sealed using paraffin under the rotor cap. Thus prepared samples can be stored in air for more than 24 h without noticeable changes.

## 3. Results and discussion

Table 1 shows the  $^{27}\text{Al}$  NMR chemical shifts,  $\delta$ , of the hexane OAC solutions, toluene  $\text{AlCl}_3$  solution and solid  $\text{AlCl}_3$ . The values obtained agree well with the literature data [6,9]. In solutions OAC and  $\text{AlCl}_3$  exist as dimers, Al being in the tetrahedral coordination. The  $^{27}\text{Al}$  NMR chemical shifts (96–169 ppm) depend on the nature of the ligand. Comparison of the chemical shifts of  $\text{AlCl}_3$ ,  $\text{AlEtCl}_2$ , and  $\text{AlEt}_2\text{Cl}$  solutions shows that as an organic ligand re-



Scheme 1. A possible structure of the  $\text{AlCl}_3$  monomer complex on  $\text{MgCl}_2$  (100) face.

Table 1  
 $^{27}\text{Al}$  NMR chemical shifts of compounds  $\text{AlEt}_3-n\text{Cl}_n$

Compound	$\text{AlEt}_3$	$\text{AlEt}_2\text{Cl}$	$\text{AlEtCl}_2$	$\text{AlCl}_3$	$\text{AlCl}_3$ crystalline
Solvent	hexane	hexane	hexane	toluene	—
Chem. shift (ppm)	155	169	129	96	-3

places an inorganic one in compounds with the same Al coordination, the line shifts to lower field (chemical shift increases). On the other

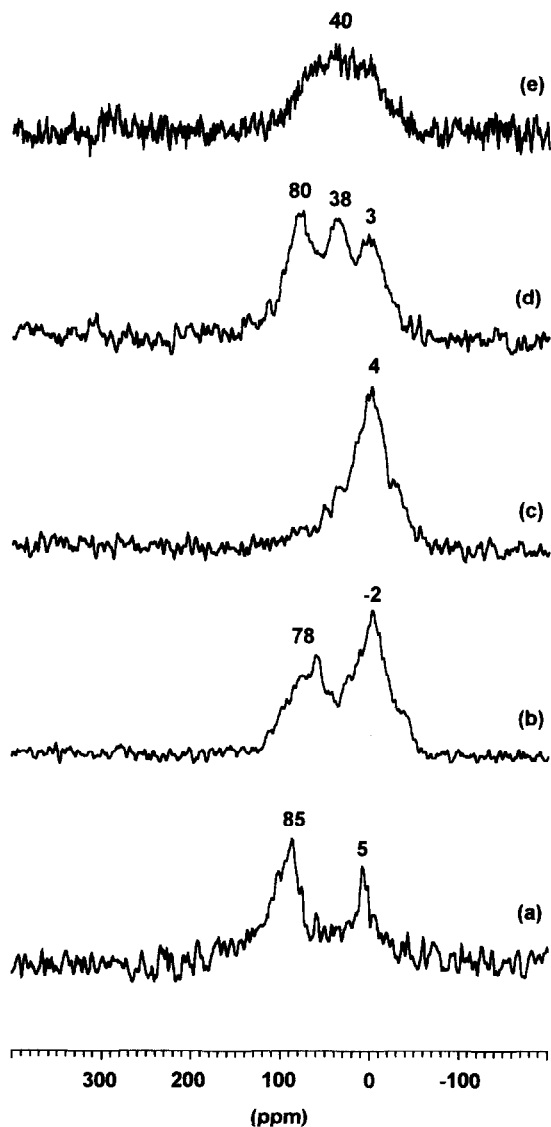
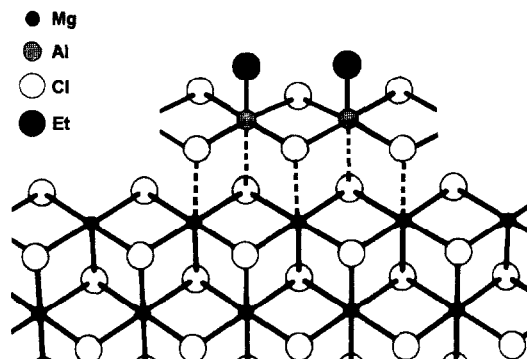
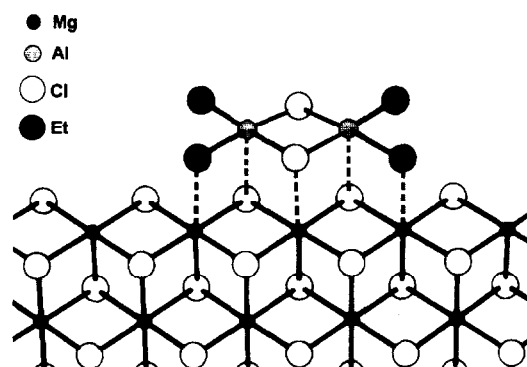


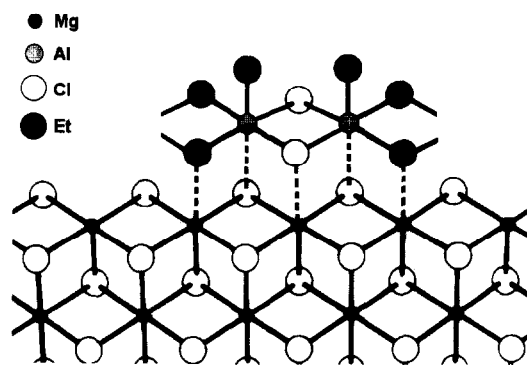
Fig. 1.  $^{27}\text{Al}$  NMR MAS spectra of (a)  $\text{AlCl}_3/\text{MgCl}_2$  (0.31 wt% of Al) (b)  $\text{AlCl}_3/\text{MgCl}_2$  (3.6 wt% of Al) (c)  $\text{AlEtCl}_2/\text{MgCl}_2$  (0.70 wt% of Al) (d)  $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$  (0.68 wt% of Al) (e)  $\text{AlEt}_3/\text{MgCl}_2 + \text{Bu}_2\text{O}$  (1:1) (0.65 wt% of Al).



Scheme 2. A possible structure of  $\text{AlEtCl}_2$  chains on  $\text{MgCl}_2$  (100) face.



Scheme 3. A possible structure of the  $\text{AlEt}_2\text{Cl}$  dimer complex on  $\text{MgCl}_2$  (100) face.



Scheme 4. A possible structure of  $\text{AlEt}_2\text{Cl}$  chains on  $\text{MgCl}_2$  (100) face.

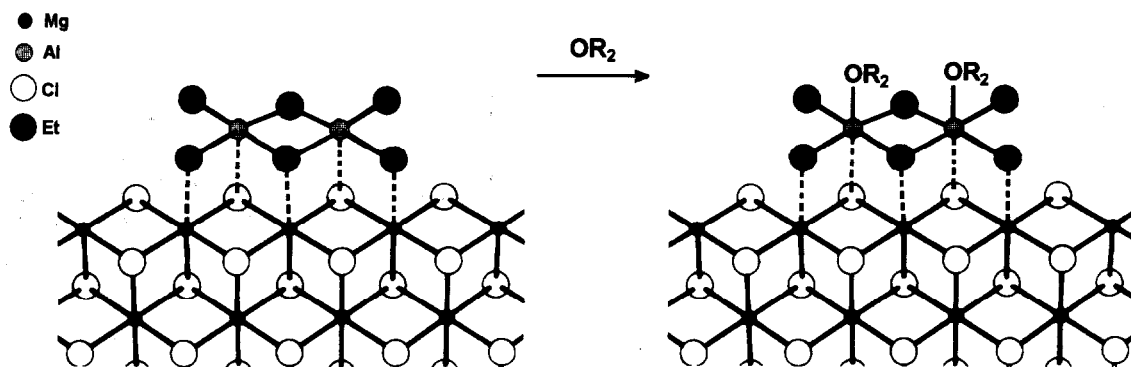
hand, as the Al coordination number increases (up to six in crystalline  $\text{AlCl}_3$ ), the chemical shift decreases. Similar correlations are likely to occur in the supported Al complexes forming on the  $\text{MgCl}_2$  surface. A priori, as Al compound interacts with the surface chlorine, its coordination number increases, and thus the chemical shift of the adsorbed state should decrease in comparison to that of the dissolved state.

Fig. 1a shows the  $^{27}\text{Al}$  NMR MAS spectrum of sample  $\text{AlCl}_3/\text{MgCl}_2$  (0.31 wt% Al). It exhibits a main line at 85 ppm and a low-intensity line at 5 ppm. The line at 85 ppm corresponds to 4-coordinated Al surrounded by chlorine atoms. Such a structure can form when  $\text{AlCl}_3$  adsorbs as a monomer on the  $\text{MgCl}_2$  (100) face (Scheme 1). The line at 5 ppm can be attributed to small amounts of  $\text{AlCl}_3$  with 6-coordinated Al. The 6-coordinated Al, symmetrically surrounded by chlorine atoms (solid non-aqueous  $\text{AlCl}_3$ ), has an  $^{27}\text{Al}$  NMR MAS line at  $-3$  ppm (Table 1). Indeed, the intensity of the line of the 6-coordinated Al increases significantly, following the increase of the  $\text{AlCl}_3$  content on the  $\text{MgCl}_2$  surface (Fig. 1b).

Fig. 1c shows the  $^{27}\text{Al}$  NMR MAS spectrum of sample  $\text{AlEtCl}_2/\text{MgCl}_2$ . The line at 4 ppm in the spectrum should be attributed to 6-coordinated Al complexes, comprising one ethyl group and five chlorine atoms in the first coordination sphere. Such Al complexes can form due to the adsorption of  $\text{AlEtCl}_2$  on the  $\text{MgCl}_2$  (100) face as  $(\text{AlEtCl}_2)_m$  chains (Scheme 2).

The  $^{27}\text{Al}$  NMR MAS spectrum of sample  $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$  is shown in Fig. 1d. It consists of a superposition of three lines at 80, 38 and 3 ppm. Since Al in the tetrahedral chlorine environment has a chemical shift of ca. 100 ppm, similarly coordinated Al but with two ethyl ligands should exhibit higher chemical shifts ( $\sim 140$ – $120$  ppm) [6]. Therefore, the line at 80 ppm (Fig. 1d) can be attributed to the 5-coordinated Al with two ethyl groups, for example, in the dimer complexes on the  $\text{MgCl}_2$  (100) face (Scheme 3). The line at 38 ppm can arise from 6-coordinated Al in the  $(\text{AlEt}_2\text{Cl})_m$  chains forming on the  $\text{MgCl}_2$  surface (Scheme 4). The line at 3 ppm most likely corresponds to the 6-coordinated Al with 4 chlorine atoms and 2 ethyl groups in the first coordination sphere.

We failed to obtain the  $^{27}\text{Al}$  NMR MAS spectrum for sample  $\text{AlEt}_3/\text{MgCl}_2$ , although the Al content was as in the previous samples. Perhaps it results from some peculiar behavior of the  $^{27}\text{Al}$  nucleus in the solid state NMR.  $^{27}\text{Al}$  has a nuclear spin of  $I = 5/2$  and a high nuclear quadrupole moment. Therefore, in the case of  $^{27}\text{Al}$  sites with a strongly distorted environment the strong quadrupole interactions result in too broad lines that can not be observed in the spectrum [5]. Only a certain fraction of Al (in a more or less regular environment) can be detected in the  $^{27}\text{Al}$  NMR experiments. Besides, the failure of NMR spectroscopy in this case can be caused by a large number of various adsorbed  $\text{AlEt}_3$  complexes, each individual



Scheme 5. Formation of a 6-coordinated aluminum complex in the  $\text{AlEt}_3/\text{MgCl}_2$  system after ether adsorption.

complex being beyond the NMR sensitivity threshold.

In order to test Al coordination, we treated this sample with dibutyl ether ( $C_4H_9$ )<sub>2</sub>O in hexane at room temperature (molar ratio ether/ $AlEt_3 = 1$ ). A thus treated sample gives a NMR spectrum with a satisfying signal/noise ratio (Fig. 1e). It has a wide line at 20–50 ppm that is a superposition of the lines from different Al complexes. Judging from the line position, we can attribute it to 6-coordinated Al surrounded by organic (Et) and inorganic (Cl, O from  $Bu_2O$ ) ligands. Such complexes with a higher symmetry (registered by NMR) can form when ether molecules are coordinated on the surface compounds  $AlEt_3/MgCl_2$  with a lower symmetry of the Al environment (for example, see Scheme 5).

#### 4. Conclusion

The surface compounds formed upon OAC deposition on highly dispersed  $MgCl_2$  were identified by  $^{27}Al$  NMR MAS. The results obtained indicate aluminum forms surface complexes with the Lewis sites of the support (magnesium and chlorine ions). As the aluminum compound adsorbs until the surface is saturated, the coordination number of Al increases. Pre-

dominantly 5- and 6-coordinated Al compounds form as dimers and chains. In the case of  $AlCl_3$ , until the content of adsorbed  $AlCl_3$  is less than the number of Lewis acid centers on the  $MgCl_2$  surface, Al remains mainly in the 4-coordinated state. So, the monomer form of  $AlCl_3$  takes part in the adsorption. It has been shown that it is possible to test the structure of unsaturated surface aluminum complexes using an electron-donor compound, which increases the aluminum coordination number. In particular, dibutyl ether adsorption increases the Al coordination number in  $AlEt_3/MgCl_2$ .

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