

^{27}Al NMR MAS study of the surface Al complexes formed in reaction of organoaluminium compounds with supported $\text{TiCl}_4/\text{MgCl}_2$ catalyst

A.G. Potapov ^{*}, V.V. Terskikh, V.A. Zakharov, G.D. Bukatov

Boreskov Institute of Catalysis, Prospekt Akademika Lavrentieva, 5, 630090, Novosibirsk, Russian Federation

Received 4 August 1998; accepted 16 November 1998

Abstract

^{27}Al NMR MAS method has been used to study the surface aluminium compounds forming during the treatment of supported $\text{TiCl}_4/\text{MgCl}_2$ catalyst with organoaluminium compounds (OAC) of various composition (AlEt_3 , AlOct_3 , AlEt_2Cl). Dialkylaluminium chloride has been found to be the main surface compound in the case of trialkylaluminium. Three surface species of dialkylaluminium chloride have been identified: one of them corresponds to 5-coordinated aluminium; the other two correspond to 6-coordinated aluminium with different alkyl-to-chlorine ratio. The relative amounts of surface species depend on the conditions of OAC reaction with catalysts and OAC composition. After polymerization of ethylene or propylene on trioctylaluminium-treated catalysts (polymer yield ca. 1 g/1 g catalyst), the signals of 5-coordinated aluminium disappear from the ^{27}Al NMR spectra of the catalysts. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: ^{27}Al NMR MAS; Supported Ziegler–Natta catalysts; Olefin polymerization

1. Introduction

Titanium tetrachloride, TiCl_4 , adsorbed on the surface of highly dispersed MgCl_2 is an active component of supported titanium–magnesium catalysts for olefin polymerization. Active sites of these catalysts are formed at the reaction of the $\text{TiCl}_4/\text{MgCl}_2$ with co-catalyst, usually AlEt_3 and $\text{Al}(i\text{-Bu})_3$. The co-catalyst reduces supported TiCl_4 into TiCl_3 with its

subsequent alkylation, with the aluminium containing compounds adsorbing tightly on the catalyst surface [1,2]. The composition of organoaluminium co-catalyst affects essentially a performance of the catalyst kinetic and stereospecificity of the propylene polymerization [3–5]. For example, supported titanium–magnesium catalysts with dialkylaluminium chloride as co-catalyst demonstrate no polymerization activity [3,5].

Several possible structures of the active component and active centers of supported titanium–magnesium catalysts are suggested in the literature [1,6–9]. However, reliable experimen-

^{*} Corresponding author. Fax: +7-383-2-343-056; E-mail: potapov@catalysis.nsk.su

tal data in favor of any one of these structures are still lacked. In particular, the role of aluminium compounds formed on the catalyst surface after the catalyst reaction with organoaluminium co-catalyst has yet to be determined. Previously, with the use of ^{27}Al NMR MAS spectroscopy, we have identified the surface complexes of various OAC adsorbed on highly dispersed magnesium chloride [10]. In the present work, we have used ^{27}Al NMR MAS to study surface species formed in the reaction of OAC with supported $\text{TiCl}_4/\text{MgCl}_2$ catalyst.

2. Experimental

Titanium–magnesium catalyst (TMC, 0.6 wt.% Ti) was obtained by supporting TiCl_4 on highly dispersed MgCl_2 ($S_{\text{BET}} \sim 76 \text{ m}^2/\text{g}$) in heptane at room temperature and washing with hexane. Highly dispersed MgCl_2 support was obtained via the reaction of Mg powder with butyl chloride (molar ratio $\text{BuCl}/\text{Mg} = 3$) in hexane at 68°C [11].

Heptane solutions of AlEt_3 , AlEt_2Cl and AlOct_3 (trioctylaluminium) were used to treat the obtained catalyst. The procedure was as follows. Weighted portions of catalyst and solvent (heptane) were loaded into a glass reactor under Ar atmosphere, then OAC solution with a

concentration of 50–60 mmol/l was added at a molar ratio of $\text{Al}/\text{Ti} \approx 30\text{--}40$ under stirring, the mixture was kept at ambient temperature for 60 min. In a separate experiment this treatment continued for 3 min (Table 1, sample 1), then the obtained samples were washed with solvent and dried in vacuum.

In order to obtain samples of the catalysts with a polymer—after treatment of catalyst with OAC—the reactor at ambient temperature was fed with olefin (ethylene or propylene) amounting to ca. 1.5–2 g olefin/g catalyst (ca. 400 g/g Ti) and kept for 5 min. The samples were then washed with solvent and dried under vacuum. Polymer content in samples were calculated from the decrease in Ti content.

NMR spectra were recorded with a Bruker MSL-400 spectrometer (magnetic field 9.4 T, ^{27}Al resonance frequency 104.5 MHz) in a frequency range of 100 kHz. The number of accumulation was ca. 25 000 with a pulse width of 2 μs ($\pi/12$) and 0.2 s delay between pulses. Magic angle spinning in Andrew–Beams PMMA rotors (rotation frequency of 3–4 kHz) was applied. Chemical shifts were measured in ppm and referenced to the external 1 M aqueous solution of AlCl_3 . The accuracy of the chemical shift measurements depends on signal/noise ratio and usually attains 10% of the line width (i.e., 1–10 ppm). To avoid contact of the sam-

Table 1

Data on the content of titanium and aluminum in OAC/TMC^a samples and polymer yield

Sample No.	Composition of the sample	Ti		Al		Al/Ti, mol/mol	Polymer yield, g/g cat
		wt.%	mmol/g	wt.%	mmol/g		
1	AlEt_3/TMC , 3 min	0.50	0.104	0.40	0.148	1.42	–
2	AlEt_3/TMC	0.40	0.083	0.42	0.156	1.87	–
3	$\text{AlEt}_3/\text{TMC} + \text{PE}$	0.19	0.040	0.20	0.074	1.87	1.1
4	$\text{AlEt}_3/\text{TMC} + \text{PP}$	0.21	0.044	0.22	0.081	1.86	0.9
5	$\text{AlEt}_2\text{Cl}/\text{MgCl}_2$	–	–	0.47	0.174	–	–
6	$\text{AlEt}_2\text{Cl}/\text{MgCl}_2 + \text{AlEt}_3$	–	–	0.47	0.174	–	–
7	$\text{AlEt}_2\text{Cl}/\text{TMC}$	0.48	0.100	0.36	0.133	1.33	–
8	$\text{AlEt}_2\text{Cl}/\text{TMC} + \text{PE}$	0.30	0.063	0.30	0.111	1.78	0.6
9	$\text{AlEt}_2\text{Cl}/\text{TMC} + \text{PP}$	0.34	0.071	0.28	0.104	1.46	0.4
10	$\text{AlOct}_3/\text{TMC}$	0.40	0.083	0.38	0.141	1.69	–
11	$\text{AlOct}_3/\text{TMC} + \text{PE}$	0.20	0.042	0.20	0.074	1.78	1
12	$\text{AlOct}_3/\text{TMC} + \text{PP}$	0.18	0.038	0.19	0.070	1.88	1.2

^aThe initial TMC contains 0.6 wt.% of Ti (0.125 mmol Ti/(g cat)).

ples with air, their weighted portions (0.1–0.2 g) were loaded into the NMR rotor under Ar atmosphere and insulated with a paraffin bed under the rotor cap. Thus prepared samples can be stored in air over a day without changes of their spectra.

3. Results and discussion

Table 1 shows the data on Ti and Al content in the studied catalysts as determined by the chemical analysis.

It should be noted that the treatment of the catalyst with OAC results in decrease of Ti content. For example, samples 2, 7 and 10 contain 0.40, 0.48 and 0.40 wt.% of Ti, respectively, vs. 0.60 wt.% of Ti in the initial catalyst. Similar result has been obtained previously in Ref. [12] for $\text{TiCl}_4/\text{MgCl}_2$ catalyst treated with AlEt_3 or AlEt_2Cl at ambient temperature and molar ratio $\text{Al}/\text{Ti} = 1-2$.

Catalysts treated with different OAC contain close amounts of aluminium (0.36–0.42 wt.% of Al in samples 2, 7 and 10 in Table 1). As we demonstrated earlier [10], OAC of various composition (AlEt_3 , AlEt_2Cl and AlEtCl_2) tightly adsorb on the surface of initial MgCl_2 support. It is important that different OAC adsorb on MgCl_2 surface in close amount; so it is proposed that adsorbed OAC form surface complexes with the same Lewis acid sites of the magnesium chloride [10].

The support used in the present study can adsorb OAC in an amount of ca. 0.174 mmol/g (see sample 5, Table 1). According to Ref. [10], it is possible to suggest that TiCl_4 and OAC adsorb on the same centres of MgCl_2 surface. Therefore, in catalyst with 0.083 mmol Ti/g (sample 2, Table 1), free MgCl_2 surface centres are still available for OAC adsorption. The number of these centres can be estimated as a difference $0.174 - 0.083 \text{ mmol/g} = 0.091 \text{ mmol/g}$.

Sample 2 (TMC treated with AlEt_3) contains 0.156 mmol Al/g. If this aluminium compound

will adsorb preferentially on MgCl_2 surface (as a limit case), then it will be distributed as 0.091 mmol/g on MgCl_2 surface and 0.065 mmol/g on titanium centres. Draftly, in this sample OAC can bind with ca. 80% of titanium ions; and in sample 10 with more than 60% of titanium ions. The important conclusions of these estimations are: (i) OAC-treated catalysts contain two types of surface organoaluminium species: bonded with Ti-centres and bonded with free MgCl_2 surface; (ii) the main part of titanium ions are bonded with organoaluminium compounds.

Following are the results of ^{27}Al NMR MAS experiments. Fig. 1a shows the spectrum of the AlEt_3/TMC sample obtained after 3 min contact time of AlEt_3 with TMC. This spectrum

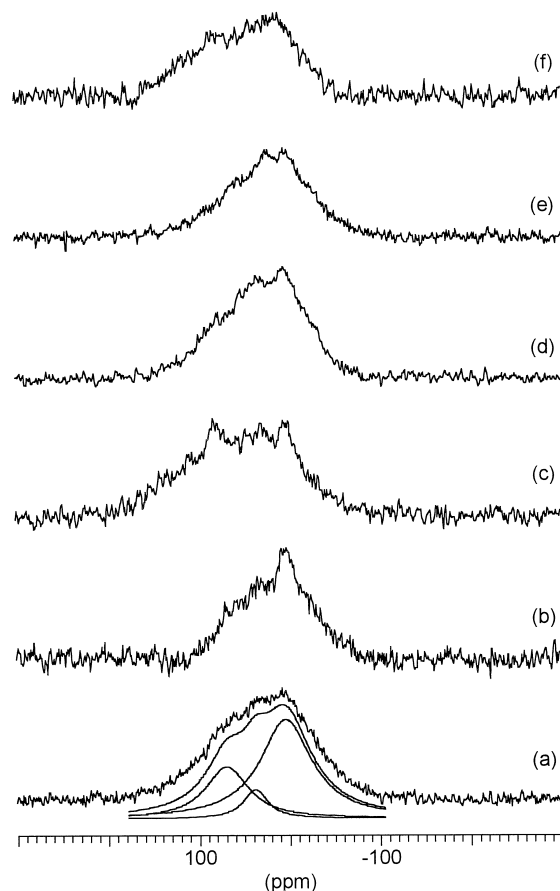


Fig. 1. ^{27}Al NMR MAS spectra of (a) AlEt_3/TMC , 3 min; (b) AlEt_3/TMC ; (c) $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$; (d) $\text{AlEt}_2\text{Cl}/\text{MgCl}_2 + \text{TEA}$; (e) $\text{AlEt}_2\text{Cl}/\text{TiCl}_3$; (f) $\text{AlEt}_2\text{Cl}/\text{TMC}$.

may be considered as a superposition of three lines (possible decomposition inserted): the more intensive line at ca. 10 ppm and two less intensive lines at 35 and 70 ppm. It is important to note that no spectra were detected for $\text{AlEt}_3/\text{MgCl}_2$ sample in Ref. [10], which seems to be due to a strongly disordered structure of surface AlEt_3 species. In contrast, the spectrum of the $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ sample (Fig. 1c and data of Ref. [10]) contains three lines, with positions close to those for the spectrum of AlEt_3/TMC sample, with somewhat different relative intensities. The similarity of the spectra seems to originate from the similarity of surface species for AlEt_3/TMC and $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ samples. This is no surprise since AlEt_3 reacts with TMC producing AlEt_2Cl . The second AlEt_2Cl molecule can be formed at the alkylation of TiCl_3 with AlEt_3 . Hence the species formed at the reaction of AlEt_3 with TMC have AlEt_2Cl composition and are strongly bonded with the catalyst surface. The structure of these species is close to that of $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ samples, that follows from the above-mentioned similarity of their NMR spectra. The attribution of the lines in these spectra was performed in Ref. [10] as follows. The line at 70–80 ppm was attributed to 5-coordinated Al with two ethyl groups. The line at 35 ppm could arise from the 6-coordinated Al with three ethyl groups in the $(\text{AlEt}_2\text{Cl})_n$ chains forming on the MgCl_2 surface. The line at 10 ppm most likely corresponds to the 6-coordinated Al with 4 chlorine atoms and 2 ethyl groups in the first coordination sphere. Note, the AlEt_3/TMC and $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ spectra differ by a relative intensity of lines: the line at ~ 70 ppm is more intensive in the spectrum of $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ (Fig. 1c).

Fig. 1b shows ^{27}Al NMR spectrum of AlEt_3/TMC (sample 2) obtained via the interaction of AlEt_3 with TMC during 1 h. Compared with sample 1 (Fig. 1a), longer reaction time resulted in the decrease of intensities of the lines at 70 ppm and 35 ppm, although the Al content in this sample did not change, as chemi-

cal analysis showed (see Table 1). Perhaps, AlEt_3 displaces the surface species with 5-coordinated Al and 6-coordinated Al with three chlorine ligands. To check this suggestion, we treated sample $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ (Fig. 1c) with a solution of AlEt_3 at molar ratio $\text{AlEt}_3/(\text{AlEt}_2\text{Cl})_{\text{surface}} = 30$ for 50 min (Table 1, sample 6). The spectrum of this sample (Fig. 1d) is similar to that in Fig. 1a. We conclude that the process of chemical exchange of the surface and dissolved Al compounds occurs in these systems. Equilibrium is shifted towards binding of AlEt_2Cl , since a priori the adsorption heat of AlEt_2Cl exceeds that of AlEt_3 . To provide a more profound displacement of AlEt_2Cl from the catalyst surface, the excess of AlEt_3 is required. Besides, catalyst surface retains the tightly adsorbed Al compound (most likely AlEt_2Cl) which coordination corresponds to the ^{27}Al NMR line at ca. 10 ppm. The time of equilibrium achievement depends on experimental conditions and seems to exceed several minutes. The above chemical analysis data confirm that in this system OAC can adsorb both on free surface centres of MgCl_2 and on TiCl_3 . It should be noted that we cannot distinguish AlEt_2Cl adsorbed on MgCl_2 from that adsorbed on TiCl_3 forming in this system. We carried out an adsorption of AlEt_2Cl on TiCl_3 so as to check the above supposition. For this purpose we treated a sample of $\alpha\text{-TiCl}_3$ ($S_{\text{BET}} = 52 \text{ m}^2/\text{g}$) with AlEt_2Cl at a molar ratio $\text{Ti}/\text{Al} = 40$ at ambient temperature. The ^{27}Al NMR spectrum of the obtained sample is shown on Fig. 1e. The position of the main line is ca. 10 ppm, which is close to one of the lines in the spectrum of $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$. TiCl_3 formed at the reduction of supported $\text{TiCl}_4/\text{MgCl}_2$ exists on the catalyst surface predominantly in a form of associates $(\text{TiCl}_3)_x$ replicating the structure of the MgCl_2 surface [12]. The coordination environment of Al in OAC adsorbed on TiCl_3 is likely to be the same, as in OAC adsorbed on MgCl_2 .

The spectrum of sample $\text{AlEt}_2\text{Cl}/\text{TMC}$ is presented on Fig. 1f. It consists of two lines—the main line at 10 ppm and a less intensive line

shifted to low field. The first line may be attributed to adsorbed AlEtCl_2 , quite likely forming in this system. It should be noted that the previously recorded spectrum of sample $\text{AlEtCl}_2/\text{MgCl}_2$ consisted of a similar line [10]. However, the main line cannot be unambiguously attributed to AlEtCl_2 , since the same line is observed in the spectrum of sample $\text{AlEt}_2\text{Cl}/\text{MgCl}_2$ (Fig. 1c). The line at 70–80 ppm seems to correspond to small amounts of adsorbed AlEt_2Cl .

Adding monomers to catalyst AlEt_3/TMC (sample 2), we obtained samples containing ca. 1 g of polymer per 1 g of catalyst (samples 2 and 4 from Table 1). Fig. 2a shows the spectra of AlEt_3/TMC before and after polymerization of ethylene. After polymerization, the spectrum of the catalyst contains a broad line with a maximum at ~ 10 ppm. The polymer formation did not practically change the ^{27}Al NMR spectrum of triethyl-treated TMC. The spectra of the samples after ethylene or propylene polymerization are close.

The spectra of the ethylene- or propylene-treated sample $\text{AlEt}_2\text{Cl}/\text{TMC}$ are the same as for the initial catalyst. It should be noted that the AlEt_2Cl system produced half as many polymer (0.4–0.6 g/g cat) as the AlEt_3 system

did, polymerization conditions being the same (Table 1).

The spectrum of sample $\text{AlOct}_3/\text{TMC}$ (Fig. 2b) is similar to that of AlEt_3/TMC (Fig. 1a). The lines at 70 and 35 ppm disappear from the spectrum of the sample after polymerization of ethylene (Fig. 2b). The spectra of samples $\text{AlOct}_3/\text{TMC}/\text{PE}$ and $\text{AlOct}_3/\text{TMC}/\text{PP}$ are close. A fraction of Al compounds disappeared from ^{27}Al NMR spectra after polymerization attains ca. 20% of total Al content. Possible reasons of disappearance from the ^{27}Al NMR spectra of this part of Al atoms are the removal of Al complexes from surface or disordering of Al coordination environment, as it has been observed for $\text{AlEt}_3/\text{MgCl}_2$ [10]. The spectra of samples $\text{AlOct}_3/\text{TMC}/\text{PE}$ and $\text{AlOct}_3/\text{TMC}/\text{PP}$ are similar to those of samples $\text{AlEt}_3/\text{TMC}/\text{PE}$ and $\text{AlEt}_3/\text{TMC}/\text{PP}$ (Fig. 2a).

So, we can conclude that surface dialkylaluminum chlorides Al_1 and Al_2 , corresponding to the lines at 70 and 35 ppm on the ^{27}Al NMR spectra of samples AlEt_3/TMC and $\text{AlOct}_3/\text{TMC}$, are more labile compared with surface complexes Al_3 , characterised by the line at 5–10 ppm. As the catalyst reacts with excess of AlR_3 or participates in polymerization, the lines at 70 and 35 ppm disappear from its spectrum.

We suggest that these results can be explained in the following way. Compounds Al_1 (75 ppm) and Al_2 (35 ppm) are reversibly adsorbed on the catalyst surface, including titanium trichloride—the active component of the catalyst. Active centres can be formed only after Al_1 and Al_2 desorption, for example, under the action of excess AlR_3 . Forming on the catalyst surface, the polymer inhibits reversible adsorption of dialkylaluminum chloride or disorders the coordination environment of Al in adsorbed AlR_2Cl (Al/Ti ratio in samples with polymer remains the same, see Table 1). As a result, the line corresponding to 5-coordinated Al disappears from the ^{27}Al NMR spectrum. Surface compounds Al_3 , corresponding to the line with a chemical shift of 5–10 ppm, are tightly ad-

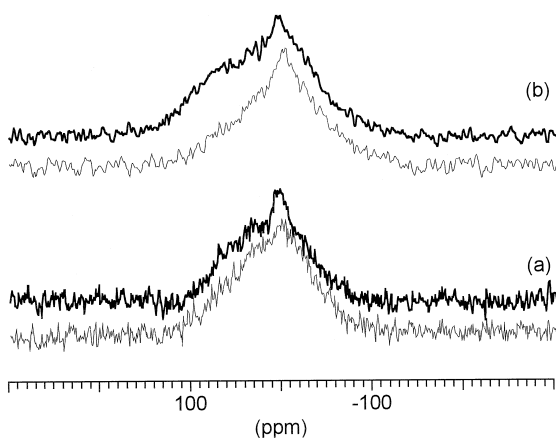


Fig. 2. ^{27}Al NMR MAS spectra of (a) AlEt_3/TMC before (thick line) and after (thin line) polymerization of ethylene; (b) $\text{AlOct}_3/\text{TMC}$ before (thick line) and after (thin line) polymerization of ethylene.

sorbed on catalyst and thus can block a significant amount of Ti ions during the whole period of polymerization.

4. Conclusion

It has been found with the use of ^{27}Al NMR that as catalyst $\text{TiCl}_4/\text{MgCl}_2$ is treated with aluminium trialkyl, the formed dialkylaluminium chloride adsorbs on catalyst surface; ^{27}Al NMR spectra demonstrate three types of surface aluminium complexes with different coordination state. The fraction of complexes of each type depends on the conditions of the interaction of catalyst with trialkylaluminium. The changes in the spectra of samples after polymerization (yield 1 g polymer/1 g cat) indicate that part of the Al compounds is removed from catalyst surface or that the coordination environment of Al in this compound became disordered. The existence of aluminium compound unremovable from the catalysts surface indicates that efforts have to be undertaken so as to prevent its formation at interaction of catalysts with co-catalyst.

Based on these results, we suppose that the portion of Ti ions in active state is governed by the process of adsorption/desorption of OAC (most likely, chlorine-containing OAC deriva-

tives), which, being adsorbed, blocks active centres. Practically, this means that excess of trialkylaluminium is required for polymerization. This suggestion explains the low co-catalytic efficiency of AlEt_2Cl in olefin polymerization.

References

- [1] P.C. Barbe, G. Cecchin, L. Noristi, *Adv. Polym. Sci.* 81 (1987) 1, and references therein.
- [2] L. Noristi, P.C. Barbe, G. Baruzzi, *Makromol. Chem.* 192 (1991) 1115.
- [3] Ye.Ye. Vermel, V.A. Zakharov, Z.K. Bukatova, G.P. Shkurina, L.G. Yechevskay, E.M. Moroz, S.V. Sydakova, *Vysokomol. Soyed. (Russ.) A* 22 (1980) 22.
- [4] Y. Doi, E. Suzuki, T. Keii, *Makromol. Chem., Rapid Commun.* 2 (1981) 293.
- [5] V.A. Zakharov, S.I. Makhtarulin, Yu.I. Yermakov, *Reaction Kinet. Catal. Lett.* 9 (1978) 137.
- [6] U. Giannini, *Makromol. Chem., Suppl.* 5 (1981) 216.
- [7] P. Corradini, V. Busico, G. Guerra, in: W. Kaminsky, H. Sinn, (Eds.), *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer-Verlag, Berlin, 1988, p. 337.
- [8] P.J.V. Jones, R.J. Oldman, in: W. Kaminsky, H. Sinn, (Eds.), *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer-Verlag, Berlin, 1988, p. 223.
- [9] A.G. Potapov, V.V. Kriventsov, D.I. Kochubey, G.D. Bukatov, V.A. Zakharov, *Macromol. Chem. Phys.* 198 (1997) 3477.
- [10] A.G. Potapov, V.V. Terskikh, G.D. Bukatov, V.A. Zakharov, *J. Mol. Cat. A: Chem.* 122 (1997) 61.
- [11] USSR Pat. 726702 (1978), invs.: V.A. Zakharov, S.I. Makhtarulin; *Chem. Abstr.* 95, 220579x (1981).
- [12] V.A. Zakharov, S.I. Makhtarulin, V.A. Poluboyarov, V.F. Anufrienko, *Makromol. Chem.* 185 (1984) 1781.