

^{27}Al MAS NMR study of the interaction of supported Ziegler–Natta catalysts with organoaluminium co-catalyst in the presence of donors

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Abstract

^{27}Al MAS NMR spectroscopy has been used to study the surface aluminium compounds formed upon interaction of the supported $\text{TiCl}_4/\text{donor}/\text{MgCl}_2$ catalyst with AlEt_3 in the presence or absence of the external donor. Similarly with the catalyst without any donors [A.G. Potapov, V.V. Terskikh, V.A. Zakharov, G.D. Bukatov, *J. Mol. Catal. A: Chem.*, 145 (1999) 147], the AlEt_2Cl formed adsorbs on the catalyst surface. It was found that there is no influence of internal and/or external donors on the state of aluminium in adsorbed AlEt_2Cl in spite of a decrease of the aluminium content in the presence of external donor. © 2000 Elsevier Science B.V. All rights reserved.

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

1. Introduction

We have studied recently by ^{27}Al MAS NMR spectroscopy the state of surface aluminium complexes formed upon interaction of AlEt_3 (co-catalyst) with the supported catalyst $\text{TiCl}_4/\text{MgCl}_2$ in the absence of any donor [1]. It was found that the main surface compound of aluminium in this case is likely to be AlEt_2Cl , the major part of aluminium being in sixfold coordination. In addition, adsorbed AlEt_2Cl was found to block a significant part of the titanium ions on the catalyst surface [1].

The $\text{TiCl}_4/\text{MgCl}_2$ catalyst itself has low stereospecificity for the polymerization of pro-

pylene. To improve the stereospecificity of the catalyst, internal donors (ID, added during catalyst preparation) and external donors (ED, added during polymerization) are used. The treatment of the catalyst containing ID by AlEt_3 co-catalyst results in a decrease of the ID content and in the appearance of aluminium in the catalyst [2,3]. When presented ED replaces ID in the catalyst and content of aluminium in the catalyst decreases. This decrease probably indicates that ED competes with AlEt_3 for the catalyst surface [3]. One can, thus, propose that the presence of ID and ED in stereospecific catalytic systems for the polymerization of propylene influences the state and/or concentration of surface aluminium-containing compounds.

The aim of the present work is to study by ^{27}Al MAS NMR spectroscopy the influence of

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ID and ED on the state and concentration of the adsorbed Al complexes.

2. Experimental

The titanium–magnesium catalysts (A) and (B) with composition of $\text{TiCl}_4/\text{ID}/\text{MgCl}_2$ (where ID is dibutylphthalate (DBP) for catalyst (A) and 2,2-diisobutyl-1,3-dimethoxypropane (DIBDMP) for catalyst (B)) were obtained as follows. Catalyst (A) was prepared via the interaction of magnesium ethoxide with a mixture of TiCl_4 and PhCl (molar ratio 1:1) in the presence of DBP at 115°C with subsequent washing by heptane. The catalyst contained 2.0 wt.% of Ti and 19.8 wt.% of DBP. Catalyst (B) was obtained from $\text{MgCl}_2 \cdot 3\text{ROH}$ as described earlier [4]. Catalyst (B) contained 2.9 wt.% of Ti and 13.2 wt.% of DIBDMP.

Both catalysts were treated as follows. The solvent (heptane) was loaded into a glass reactor under Ar atmosphere and an AlEt_3 solution in heptane was then introduced to attain AlEt_3 concentration of 20 or 30 mmol/l, and a molar Al/Ti ratio of 6 or 10 (see Table 1). Propyltrimethoxysilane (PTMS) was added to achieve a molar Si/Al ratio of 0.2 or 0.05 (see Table 1). Weighted portions of catalysts were introduced into the reactor under stirring and the reaction

was effected at ambient temperature for 1 h. The obtained samples were then washed several times with heptane and dried in vacuum.

The contents of Ti and Al in the samples were determined by AES-ICP technique (atomic-emission spectrometry-inductively coupled plasma).

The procedure of the ^{27}Al MAS NMR measurements was described before [5]. NMR spectra were recorded with a Bruker MSL-400 spectrometer (^{27}Al resonance frequency of 104.5 MHz) with a pulse width of 2 μs ($\pi/12$) and 0.2 s delay between pulses. Typical number of accumulations was ca. 200,000–220,000 with an exception made for sample 2, when 40,000 FIDs were accumulated.

3. Results and discussion

Table 1 shows the conditions used in the sample preparations and gives the Ti and Al contents of the studied catalysts. The ^{27}Al NMR MAS spectra of the catalysts are presented in Fig. 1.

Treatment of catalyst (A) by AlEt_3 with a molar ratio Al/Ti = 6 did not change the catalyst composition with respect to the Ti and donor contents (Table 1, sample 1). The ^{27}Al MAS NMR spectrum of this sample (Fig. 1-1)

Table 1
Conditions of samples preparation and their compositions according to analytical analysis

Sample no.	Treatment conditions			Sample compositions				
	[AlEt_3] (mmol/l)	Al/Ti (mol/mol)	Si/Al (mol/mol)	Ti (wt.%)	Al (wt.%)	Mg (wt.%)	Donor ^a (wt.%)	Al/Ti (mol/mol)
Cat. A	–	–	–	2.00	–	18.3	19.8	–
Cat. B	–	–	–	2.90	–	19.1	13.2	–
1 (A)	20	6	0	2.10	1.20	17.4	19.2	1.10
2 ^b (B)	20	6	0	2.90	1.30	17.9	13.0	0.80
3 (A)	30	10	0	1.55	1.70	18.4	14.6	1.95
4 (A)	20	6	1:5	2.15	1.10	17.8	17.8	0.90
5 ^c (A)	20	6	1:5	2.00	1.15	17.6	18.7	1.05
6 (A)	30	10	1:20	1.65	1.40	18.3	16.0	1.50

^a Calculated from data on Ti (as TiCl_3), Al (as AlEt_2Cl) and Mg (as MgCl_2) contents up to a total of 100%.

^b Catalyst B with DIBDMP as internal donor was used.

^c The sample was first treated by AlEt_3 (1 h), then PTMS was added, and the treatment was pursued for one more hour.

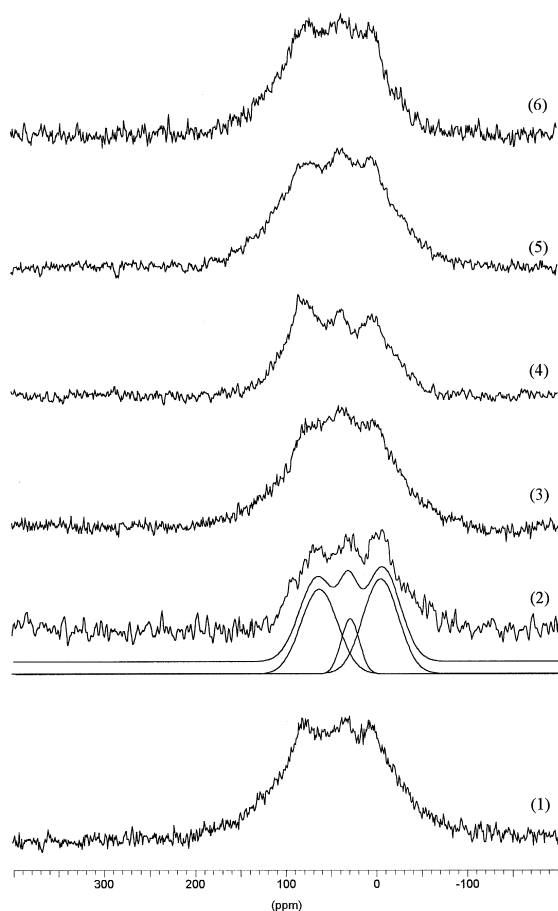


Fig. 1. ^{27}Al MAS NMR spectra of the studied samples. The spectra are labeled according to Table 1.

consists of the superposition of three lines: two lines of comparable intensities at ca. 5 ppm and ca. 70 ppm and a smaller line at 35 ppm. This spectrum arises from AlEt_2Cl adsorbed at the catalyst surface [1]. The attribution of these lines in such spectra was discussed previously [5], the lines at 5 and 35 ppm correspond to Al in sixfold coordination and the line at 70 ppm to Al in fivefold coordination.

As the molar Al/Ti ratio is close to 1 in sample 1 (Table 1) and since there is no significant removal of ID from the surface of the catalyst, the AlEt_2Cl , which is formed, adsorbs mainly on TiCl_3 formed at the reduction of TiCl_4 . This result is supported by the data obtained for catalyst (B) containing the ID which

is not removable by AlEt_3 (Table 1, sample 2; Fig. 1-2). It is interesting to note that the quantity of Lewis acidic sites in this sample (as measured by adsorption of stable nitroxyl radical) was about a quarter of the titanium content [4]. This value is close to the molar content of adsorbed AlEt_2Cl in which Al is fivefold coordinated (ca. 40%, as measured by NMR-spectrum deconvolution, Fig. 1-2) and accounts for ca. 30% of the total titanium content. This species is probably responsible for the Lewis acidic properties.

The treatment of catalyst (A) by AlEt_3 at molar ratio Al/Ti of 10 (sample 3) resulted in a decrease of both the titanium and donor contents in the catalyst and in the incorporation of a larger amount of aluminium-containing compounds relative to sample 1. The ^{27}Al MAS NMR spectrum (Fig. 1-3) of this catalyst resembles the spectra of samples 1 and 2 in spite of the significant changes of the composition. The molar aluminium content is twice higher than the titanium content although the titanium content is only decreased by 25% (Table 1, sample 3). It is interesting to note that the content of aluminium (0.63 mmol/g) exceeds that of titanium (0.32 mmol/g) by a quantity of removed TiCl_4 (0.10 mmol/g) and ID (0.19 mmol/g). Perhaps, the formed AlEt_2Cl adsorbs both on TiCl_3 and MgCl_2 surface centres which are formed after removal of some titanium compounds and of the ID by reaction with AlEt_3 . Similar results were obtained in Ref. [3]: the aluminium content in the catalyst treated by AlEt_3 increased in parallel with a decrease of ID content to reach the same or higher Al/Ti ratio compared to those of the catalyst without ID [2].

We conclude, therefore, that in the case of the catalyst containing an ID, the states of aluminium in the surface Al complexes are similar to those observed in the catalyst without ID. The higher intensity of the line at 70 ppm (Fig. 1-1) relative to that for the catalyst $\text{TiCl}_4/\text{MgCl}_2$ reported in Ref. [1] seems to be accounted for by the lower Al/Ti ratio used

during the preparation of sample 1. As it was shown in Ref. [1], an excess of AlEt_3 resulted in the removal of AlEt_2Cl complexes in which Al is in fivefold coordination.

The introduction of ED at the treatment of the catalyst (A) by AlEt_3 did not change noticeably the composition of the catalyst (Table 1, samples 4 and 1). The Al/Ti molar ratio of the catalyst decreases only by $\sim 20\%$. A small decrease of donor content (wt.%) can be accounted for by the replacement of DBP by PTMS which has a smaller molecular weight. The ^{27}Al MAS NMR spectrum of this sample (Fig. 1-4) differs from the spectrum of sample 1 only by a somewhat higher intensity of the line at 70 ppm. It may be that the effective concentration of AlEt_3 in this preparation was lower (compared with sample 1) because of its complexation with PTMS, thus decreasing the removal of AlEt_2Cl (with Al in fivefold coordination) from the catalyst surface.

Sample 5, obtained by AlEt_3 treatment of catalyst (A) with subsequent addition of PTMS, did not differ noticeably by its composition from sample 1 (Table 1). The addition of PTMS does not influence the state of Al in the surface complexes: the ^{27}Al MAS NMR spectrum of this sample (Fig. 1-5) is similar to that obtained for sample 1 (Fig. 1-1). Thus, AlEt_2Cl also interacts with TiCl_3 species formed by the reduction of TiCl_4 . Therefore, it is most likely that the surface aluminium compounds formed by the interaction of the catalyst with AlEt_3 are inert with respect to the ED used.

Sample 6 was prepared from catalyst (A) by adding of PTMS, under conditions similar to that used for sample 3 (Table 1). In these conditions, there are marked changes in the composition of the initial catalyst (compare sample 6 to samples 1 and 4). The content of Al and the Al/Ti molar ratio are noticeably lower

than the corresponding values for sample 3. Nevertheless, the state of the surface Al species in samples 6 and 3 remains the same (Fig. 1-6). Therefore, we conclude that an ED does not influence the state of aluminium, but can decrease the aluminium content as a result of its adsorption on MgCl_2 centres which are formed upon removal of the internal donor by AlEt_3 .

4. Conclusions

The presence of ID and ED in stereospecific catalytic systems for the polymerization of propylene does not influence the state of the surface aluminium-containing compounds (AlEt_2Cl) formed at the treatment of the catalyst by AlEt_3 . The ED does not remove AlEt_2Cl from the catalyst surface but competes with the aluminium compounds for the MgCl_2 adsorption centres which become available after the removal of the ID by AlEt_3 .

Acknowledgements

We wish to thank two anonymous reviewers for valuable comments and improvement of the manuscript.

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