The metallocene/methylaluminoxane catalysts formation: EPR spin probe study of Lewis acidic sites of methylaluminoxane

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Abstract

Using stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) as a spin probe, Lewis acidic sites of methylaluminoxane (MAO) were identified. It was found that MAO contains two types of acidic sites. TEMPO, coordinated to the sites I and II, exhibits in the EPR spectra triplet ($g_o = 2.0047$, $a_N = 18.6$ G) and triplet of sextets ($g_o = 2.0045$, $a_N = 19.6$ G and $a_{Al} = 1.7$ G), respectively (a_N and a_{Al} are constants of hyperfine structure from the corresponding nucleus). According to EPR measurements, concentration of sites I is close to that of sites II, and MAO contains one site of each type per 100 ± 30 aluminium atoms. The adducts of TEMPO with sites I are less stable than those with sites II. Based on the values of a_{Al} and relative stabilities of the adducts with TEMPO, the acidic sites I and II were attributed to coordinatively unsaturated aluminium atoms in $AlOMe_2$ and AlO_2Me environment, respectively. From the EPR spectra of coordinated TEMPO, the average radius of MAO oligomers $(AlOMe)_n$ was evaluated to be 5.8 Å at 20°C, which corresponds to the value of $n = 15$–20. Thus, the major part of MAO contains not more than one Lewis acidic site per one oligomeric $(AlOMe)_n$ molecule. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Aluminoxanes are used as co-catalysts for olefin polymerization catalysts based on the 4 group metallocenes [1–4]. There is a great interest to the catalysts of this type due to their extremely high activity and high versatility in polymer tailoring. Among all aluminoxanes, methylaluminoxane (MAO) is the most widely used co-catalyst. Much efforts have been paid to establish the nature of the active sites of the catalytic systems $[Cp_2ZrR_2 + MAO]$ (R = CH_3, Cl) and mechanism of their formation [5–8]. In spite of this, the mode of MAO to activate metallocene is not completely clear [2]. It is generally proposed that the important role of MAO is the removal of the alkyl ligand from metallocene compound with the formation of the cation-like metallocene complexes as active

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sites. MAO acts as a strong Lewis acid in this process. While species with Lewis acidity are certainly present in MAO solutions, their exact composition and structure are not still adequately understood [8]. Thus, the investigation of Lewis acidic sites of MAO, elucidation of their structure and properties are among the most interesting problems.

One of the methods of acidic sites characterization in heterogeneous catalysts is the application of spin probes (usually stable nitroxyl radicals) [9,10]. The EPR parameters of nitroxyl radical, coordinated to acidic sites of a catalyst, noticeably differs from those of free radicals and are sensitive to the acidic sites strength. This gives the instrument for the monitoring of the acidic sites of heterogeneous catalysts. In some cases, the hyperfine structure of EPR spectrum allows one to make the conclusion about TEMPO coordination to the particular atom of the catalyst's acidic site [9,10]. In homogeneous systems, the adducts of nitroxyl radicals with such Lewis acids as $AlCl_3$, $AlBr_3$, AlI_3 and $GaCl_3$ are well-known [11,12]. We have applied the spin probe technique for characterization of Lewis acidic sites of MAO using the stable nitroxyl radical 2,2,6,6-tetramethyl-piperidine-*N*-oxyl (TEMPO) as a spin probe.

2. Experimental part

2,2,6,6-Tetramethylpiperidine-*N*-oxyl (TEMPO) was purchased from Sigma and used as toluene solution (0.01 or 0.001 M). Methylaluminoxane (MAO) was purchased from Witco (Berghamen) as toluene solution (total Al content = 1.8 M, Al as $AlMe_3$ = 0.5 M). $AlEt_3$, $AlClEt_2$, $AlCl_2Et$ and $Al(i\text{-}Bu)_3$ are commercially available products, used as 0.1 M solution in hexane/toluene mixture (1:1).

Toluene was dried over molecular sieves (4 Å), purified by refluxing over sodium metal and distilled in dry argon. The distilled toluene was degassed in vacuum. The prepared solvent was stored and handled in vacuum. All experiments were carried out in sealed high-vacuum systems using breakseal techniques.

2.1. Preparation of MAO samples

MAO-1. The commercially obtained MAO was diluted with toluene to prepare a 0.1 M solution.

MAO-2 (MAO with reduced amount of $AlMe_3$). The sample of commercial MAO was distilled under vacuum. The obtained solid product (polymer MAO with residual content of $AlMe_3$, ca. 3 wt.% of Al to the total Al content) was dissolved in toluene to make a 0.1 M solution.

$AlMe_3$ solution. The liquid fraction, separated at MAO distillation, contains only $AlMe_3$ (by ^{1}H NMR data). The measured amount of this fraction was diluted with toluene to prepare ca. 0.1 M solution.

2.2. Preparation of samples for EPR investigations

The measured amount of MAO sample was cooled to $-20°C$ and mixed with appropriate amount of TEMPO solution to provide the desired MAO/TEMPO molar ratio. The prepared mixture was transferred in vacuum into cylindrical glass sample tubes, sealed off the vacuum line and used for EPR spectra registration.

2.3. EPR measurements

EPR spectra were recorded on a Bruker-200D spectrometer 9.1–9.5 GHz. Measurements were made in a sealed glass tube (diameter = 5 mm). Periclase crystal (MgO) with impurities of Mn^{2+} and Cr^{3+} which served as a side reference, was placed into the second compartment of the dual cavity. The concentration of paramagnetic centers was assessed by double integration of the EPR signal under study and of the reference sample (0.002 M toluene solution of TEMPO). EPR spectra were simulated and deconvoluted

using extended version of the EPR 1 program, described in Ref. [13].

3. Results and discussion

3.1. The interaction of TEMPO with $AlCl_2Et$ and $AlClEt_2$

The Lewis acidic sites of MAO are expected to be the coordinatively unsaturated aluminium atoms in AlO_xMe_y environment. At the first step of the investigations, we have studied the adducts of TEMPO with the model alkylaluminium compounds.

TEMPO exhibits triplet in the EPR spectrum ($g_o = 2.0055$, $a_N = 15.5$ G) due to the hyperfine structure (hfs) from nitrogen nucleus ($I = 1$, Fig. 1a). The value of hyperfine splitting (a_N) increases when TEMPO forms adducts with such Lewis acids as $AlCl_3$ ($a_N = 19$ G), $AlBr_3$ ($a_N = 19.5$ G) and AlI_3 ($a_N = 18.5$ G) [11]. Besides this, the additional hfs from aluminium nucleus ($I = 5/2$) is observed. The value of this splitting diminishes with the decrease of the acidity of the Lewis acid: $AlCl_3$ ($a_{Al} = 9.3$ G), $AlBr_3$ ($a_{Al} = 9$ G) and AlI_3 ($a_{Al} = 7.2$ G) [11].

To elucidate the influence of the alkyl ligands on the Lewis acidity of aluminium, we have investigated the interaction of TEMPO with $AlCl_2Et$ and $AlClEt_2$. According to ^{27}Al NMR data, the $AlCl_2Et$ sample used in our study contained about 20% of $AlCl_3$ as an admixture. The EPR spectrum obtained upon the interaction of TEMPO with $AlCl_2Et$ solution at molar ratio $AlCl_2Et/TEMPO = 10$ was the superposition of the EPR spectra of two adducts: $TEMPO \cdot AlCl_3$ ($g_o = 2.0050$, $a_N = 19.8$ G and $a_{Al} = 8.8$ G; [12]) and $TEMPO \cdot AlCl_2Et$ ($g_o = 2.0050$, $a_N = 19.7$ G and $a_{Al} = 6.9$ G) with relative weights 2:1 (Fig. 1b). The theoretical spectrum was in excellent agreement with the experimental one (Fig. 1b, dotted line). The width of individual lines (Lorentzian shape) used for theoretical spectrum simulation was $\sigma = 1.5$ G.
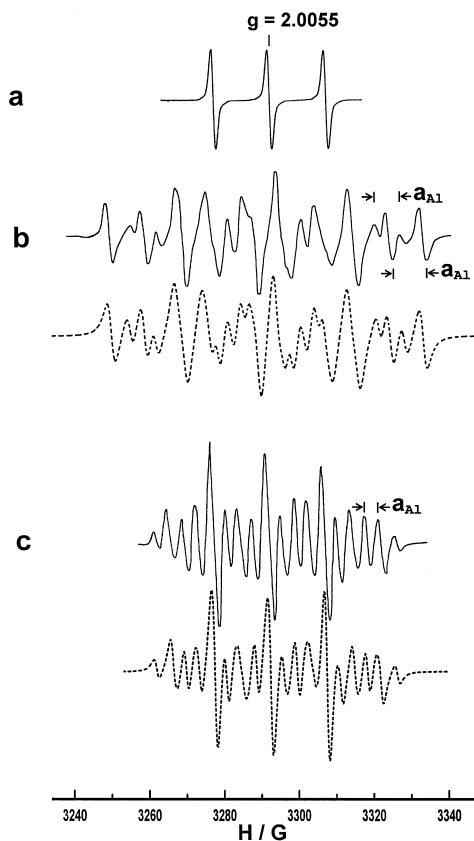

Fig. 1. EPR spectra (20°C) recorded 30 min after the onset of the reaction of TEMPO with the model alkylaluminium compounds: (a) TEMPO, (b) $AlCl_2Et/TEMPO = 10$ and (c) $AlClEt_2/TEMPO = 1$. Theoretically simulated spectra are represented by dotted lines.

The interaction of TEMPO with $AlClEt_2$ solution at molar ratio $AlClEt_2/TEMPO \approx 1$ gives rise to the EPR spectrum shown in Fig. 1c. The main features of this spectrum can be described as the superposition of the EPR spectrum of the unreacted TEMPO ($g_o = 2.0055$, $a_N = 15.5$ G and $\sigma = 1.5$ G) and that of the adduct $TEMPO \cdot AlClEt_2$ ($g_o = 2.0045$, $a_N = 19.6$ G, $a_{Al} = 3.7$ G and $\sigma = 1.5$ G). The extra two extreme lines of reduced intensity in the experimental spectrum of Fig. 1c, probably, arouse from the admixtures of alkylaluminium compounds with stronger Lewis acidity than that of $AlClEt_2$. In agreement with this assumption, EPR spectrum of Fig. 1c can be well described as the superposition of three spectra: triplet of unreacted

TEMPO, triplet of sextets with $a_N = 19.6$ G, $a_{Al} = 3.7$ G and triplet of sextets with $a_N = 19.6$ G, $a_{Al} = 5.5$ G with relative weights 3:5:2 (Fig. 1c, dotted line).

The considered adducts (Fig. 1b,c) were rather stable and their EPR spectra did not noticeably change during 1 h at room temperature. Thus, TEMPO can be used for the characterization of the Lewis acidity of alkylaluminium compounds with the composition $AlEt_xCl_{3-x}$ ($x = 1,2$). The value of a_{Al} decreases with the growth of the number of alkyl groups in the coordination sphere of aluminium. The less is the strength of the Lewis acid, the smaller is the value of the hyperfine structure from aluminium: $AlCl_3$ ($a_{Al} = 8.8$ G), $AlCl_2Et$ ($a_{Al} = 6.9$ G) and $AlClEt_2$ ($a_{Al} = 3.7$ G).

The study of the interaction of TEMPO with $AlMe_3$, $AlEt_3$ and $Al(i\text{-}Bu)_3$ showed that immediately after the onset of the reaction, EPR signal of TEMPO disappeared and no other signals were observed. Thus, AlR_3 compounds rapidly destroy the radical center of TEMPO.

3.2. The interaction of TEMPO with MAO

Commercial grade MAO that is usually used for catalytic systems preparation contains the significant amount of $AlMe_3$, associated with oligomeric molecules of MAO. This fact seems to exclude the possibility of using TEMPO to probe Lewis acidity of MAO. Fortunately, it was found that TEMPO forms with Lewis acidic sites of MAO-1 rather stable adducts (the half life time $t_{1/2} \approx 30$ min), that prevents the destruction of TEMPO radical center by $AlMe_3$. The life time of these adducts was at least four times larger for the samples of MAO-2 than for the samples of MAO-1 ($t_{1/2} \approx 2$ h). Thus, MAO-2 samples were used for further investigations.

Fig. 2a shows the EPR spectrum of the 0.02 M TEMPO solution in toluene ($g_o = 2.0055$, $a_N = 15.5$ G). Immediately after mixing of cooled ($-20°C$) TEMPO and MAO-2 solutions in toluene (at MAO/TEMPO molar ratio

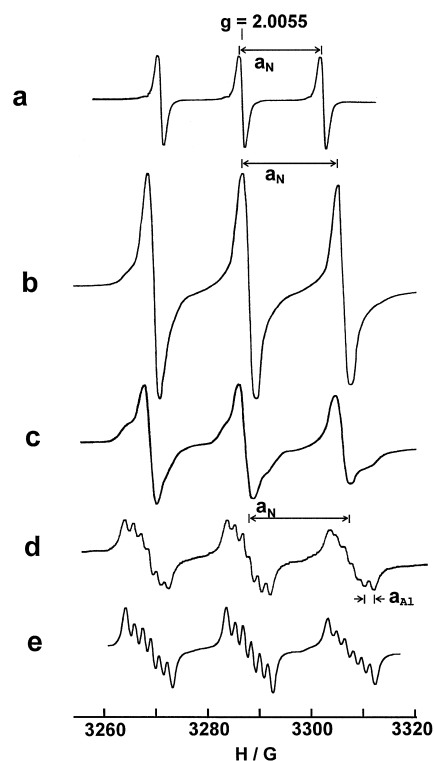Fig. 2. EPR spectra (20°C) recorded at various times after the onset of the reaction of TEMPO with MAO-2 at MAO/TEMPO = 10: (a) before the reaction, (b) at 2 min, (c) at 10 min, (d) at 20 min and (e) at 30 min.

$\alpha = 10$), the signal of TEMPO disappears and a new triplet ($g_o = 2.0047$, $a_N = 18.6$ G) was observed (Fig. 2b). The value of a_N, corresponding to the distances between the lines of triplet is larger for the new triplet than for TEMPO. Such growth of a_N is typical for the adducts of TEMPO with Lewis acids (see Section 3.1). Note, that the lines of triplet ($a_N = 18.6$ G) are twice broader than those of TEMPO (compare Fig. 2a,b). The triplet ($a_N = 18.6$ G) decreases with time ($t_{1/2} \approx 20$ min at 20°C) and the new signal (triplet of sextets, $g_o = 2.0045$, $a_N = 19.6$ G and $a_{Al} = 1.7$ G) can be clearly seen (Fig. 2c–e). The triplet of sextets slowly diminishes with time ($t_{1/2} = 3$ h at 20°C). The sextet splitting in triplet of sextets (Fig. 2d–e) is due to aluminium nucleus ($I = 5/2$, $a_{Al} = 1.7$ G). The broadening of the lines of triplet ($a_N = 18.6$ G, Fig. 2b) with respect to the lines of TEMPO can

be also caused by unresolved splitting from aluminium nucleus ($a_{Al} < 0.5$ G). The obtained data lead to the assumption that MAO contains two types of Lewis acidic sites. Further, these sites will be referred as sites I and II. TEMPO, coordinated to the sites I, exhibits triplet ($a_N = 18.6$ G) in the EPR spectra, whereas TEMPO adducts with the sites II are characterized by triplet of sextets ($a_N = 19.6$ G, $a_{Al} = 1.7$ G). The hyperfine structure from aluminium atom for triplet of sextets ($a_{Al} = 1.7$ G) is larger than that for triplet ($a_{Al} < 0.5$ G). Thus, taking into account the results obtained using the model alkylaluminium compounds, it is possible to conclude that Lewis acidity of the sites I is less than that of the sites II. The fact that the adducts of TEMPO with the sites I (triplet, $a_N = 18.6$ G) are less stable than that with the sites II (triplet of sextets) is in agreement with this conclusion. The relative integral intensities of the lines of triplet and triplet of sextets in Fig. 2b–c allow to assume that the less acidic sites I were occupied by TEMPO first and then TEMPO passed to the more acidic sites II.

The reported values of a_{Al} for TEMPO, co-ordinated to Lewis acidic sites of Al_2O_3 are 9–11 G [9,10]. Therefore, coordinatively unsaturated aluminium atoms in AlO_x environment would exhibit a_{Al} about 10 G. As it was shown earlier, the increase of alkyl groups content in the model alkylaluminium compounds resulted in diminution of a_{Al} value of EPR signal. Taking this in account, it is probable that the unsaturated aluminium atoms in $AlOMe_2$ environment constitutes the acidic sites I ($a_{Al} < 0.5$ G) and in AlO_2Me environment—the sites II ($a_{Al} = 1.7$ G). The quantitative EPR measurements show that MAO contains one site II per 100 ± 30 aluminium atoms. The adducts of TEMPO with sites I are unstable and their concentration can be determined with less accuracy than that for sites II. However, the comparison of relative integral intensities of triplet and triplet of sextets in Fig. 2a–e shows that concentrations of sites I and II with accuracy about 100% are comparable.

The EPR spectra of the samples prepared at various MAO/TEMPO molar ratio ($\alpha = 1000$–10) and recorded 30 min after the onset of the reaction at 20°C are shown on Fig. 3. It was found that the intensity of the EPR signal grows with the decrease of α value from 1000 to 100 (Fig. 3b,c), and changes insignificantly with a decrease of α from 100 to 10 (Fig. 3a,b). This result is in agreement with the content of the acidic sites II in MAO determined above. It was noted that the unstable adduct of TEMPO with the sites I (triplet, $a_N = 18.6$ G; Fig. 2b) can be observed only at the early stage of the interaction between TEMPO and MAO at high concentrations of TEMPO with respect to the concentration of Lewis acidic sites of MAO ($\alpha \sim 10$). The EPR signal of this adduct was not observed in the spectra of Fig. 3.

However, the real picture can be more complicated. The theoretical simulation of the EPR spectra of radical species, registered at various α values (Fig. 3) shows that the observed signals are the superposition of the aforementioned triplet of sextets ($g_o = 2.0045$, $a_N = 19.6$ G and $a_{Al} = 1.7$ G) and a new broadened triplet ($g_o = 2.0045$, $a_N = 19.6$ G, width of the line
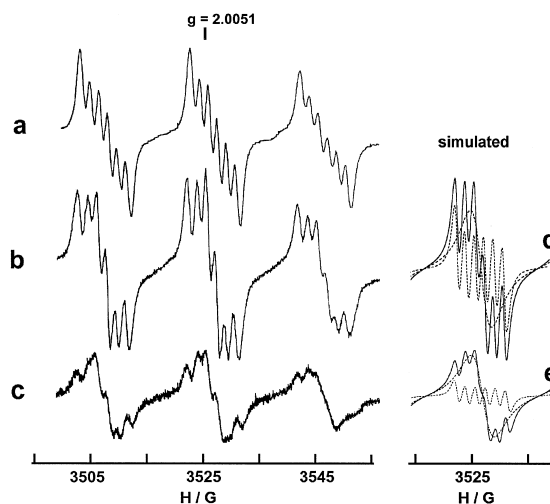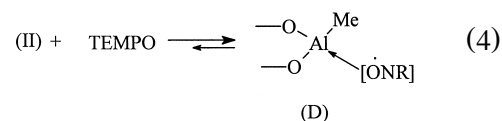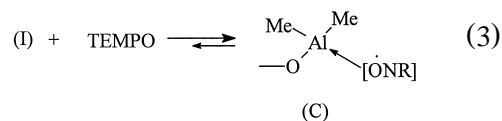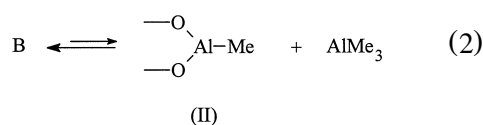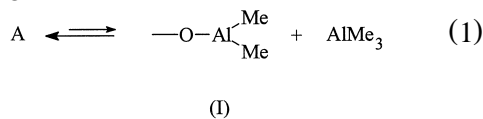

Fig. 3. EPR spectra of the samples prepared at various MAO/TEMPO molar ratios (20°C, 30 min after the onset of the reaction): (a) MAO/TEMPO = 10, (b) 100, (c) 1000, (d) the simulation of the central part of spectra b and (e) the simulation of the central part of spectra c.

$\sigma = 6$ G). The stability and EPR parameters (g_o and a_N) of this triplet are similar to those of the triplet of sextets. The theoretical simulation (Fig. 3d,e) shows that the relative weight of broadened triplet grows from $2/3$ to $7/8$ with the increase of α value from 100 to 1000, i.e., it grows with the increase of the number of Lewis acidic sites of MAO unoccupied by TEMPO. The large width of the lines of broadened triplet ($g_o = 2.0045$, $a_N = 19.6$ G) can be explained by unresolved hyperfine structure from aluminium ($a_{Al} \approx 1$ G). Alternatively, the broadened triplet with reduced value of a_{Al} can be observed if TEMPO molecule is coordinated with two Lewis acidic sites II ($a_{Al} = 1.7$ G) simultaneously, or if it is in the exchange between these two sites. However, the possibilities of such coordination or exchange are debatable and the nature of the broadened triplet is still unclear.

When the real structure of Lewis acidic sites in MAO molecule is discussed, it should be noted that MAO-2 sample used for the investigation contained ca. 3 wt.% of Al as TMA. We suppose that the Lewis acidic sites I and II of MAO are occupied by TMA to form the adducts (A) and (B):

(A)   (B)
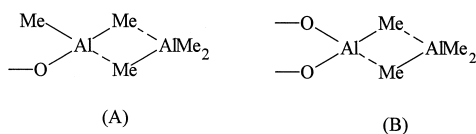
In this case, TEMPO interaction with the acidic sites I and II can be described by the following scheme (reactions 1–4):

$$A \;\rightleftharpoons\; \text{—O—Al}\begin{smallmatrix}Me\\Me\end{smallmatrix} \;+\; AlMe_3 \qquad (1)$$

(I)

$$B \;\rightleftharpoons\; \begin{smallmatrix}\text{—O}\\\text{—O}\end{smallmatrix}Al\text{—Me} \;+\; AlMe_3 \qquad (2)$$

(II)

$$(I) \;+\; TEMPO \;\rightleftharpoons\; \qquad (3)$$

(C)

$$(II) \;+\; TEMPO \;\rightleftharpoons\; \qquad (4)$$

(D)

where [ONR] = TEMPO.

We suppose that the adduct (A) formed via TMA interaction with the less acidic sites (I) is less stable than the adduct (B). In this case, the equilibrium of the reaction (1) will be more shifted to the right when compared with the reaction (2), and TEMPO will interact with the less acidic sites (I) first via the reaction (3) with the formation of adduct (C), as it was observed in the experiment. According to this scheme, in the case of the MAO-2 sample, the destruction of TEMPO by TMA occurs due to the interaction of 'free' TMA (reactions 1 and 2) with 'free' TEMPO, formed in the course of the dissociation of adducts (C) and (D) (reactions 3 and 4).

3.3. The evaluation of MAO oligomers' size from the EPR spectra of coordinated TEMPO

It is known that TEMPO coordination with large molecules causes the changes in the relative widths and intensities of the lines in its EPR spectrum, due to the decrease of the rotation correlation time τ_c. The value of τ_c and, thus, the size of the rotating molecule can be estimated from the analysis of the width of the lines in the EPR spectrum [14,15]. In our case, the EPR spectrum of the adduct of TEMPO with sites II of MAO (Fig. 2e) exhibits triplet of sextets. The widths and intensities of three sextets are different. For the high-field sextet, the

relative broadening of individual lines was $\sim$ 0.3 G; using the approaches described in [14,15], the corresponding value of $\tau_c \sim 2.0 \times 10^{-10}$ s was obtained. The similar value was obtained from the relative intensities of the sextets. Using the determined value of τ_c, the average radius of MAO oligomers (R) can be evaluated from the equation

$$\tau_c = \frac{4}{3}\frac{\pi R^3 \eta}{kT},\tag{5}$$

where η is the viscosity of the solution. Thus determined value of R was 5.8 Å.

In our previous work [16] by means of ^{13}C, ^{27}Al and ^{17}O NMR spectroscopy, the structure of MAO was investigated and it was suggested that MAO oligomers have a cage structure similar to those of cage aluminoxanes $[(t\text{-Bu})Al(\mu_3\text{-}O)]_6$ and $[(t\text{-Bu})Al(\mu_3\text{-}O)]_9$ [17,18]. The R value was evaluated as 7 Å, which corresponds to $[MeAlO]_n$ oligomers with $n = 20$–30. The R value estimated from EPR data (5.8 Å) is in a reasonable agreement with that determined from ^{27}Al NMR data. The corresponding n value of $[MeAlO]_n$ oligomers was evaluated as 15–20.

Note, that according to quantitative EPR measurements, MAO contains one Lewis acidic site I or II per 100 ± 30 aluminium atoms. Thus, it is very likely that not every oligomeric molecule of MAO contains the Lewis acidic sites and the major part of MAO contains not more than one Lewis acidic site per one oligomeric molecule.

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