

Preparation of Aryloxy-aluminoxanes and Their Use as Activators in the Bis(imino)pyridyl Iron-catalyzed Oligomerization of Ethylene

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Abstract In this study, a series of aryloxy-aluminoxanes originated directly from the hydrolysis of reaction products of AlMe_3 and phenols were synthesized, which could serve as effective polymer-retarding activators for the iron-catalyzed ethylene oligomerization. The molar ratios of $[\text{PhOH}]/[\text{AlMe}_3]$ and $[\text{H}_2\text{O}]/[\text{Al}]$ during the preparation were explored and their impacts on the oligomerization activity and product distribution were discussed. To obtain the effective activators with good polymer-retarding effect and relatively high activity, the optimized conditions were proposed to be $[\text{PhOH}]/[\text{AlMe}_3] = 0.5$ and $[\text{H}_2\text{O}]/[\text{Al}] = 0.7$. Various aluminoxanes with different $[-\text{OH}]$ sources confirmed the importance of using phenols in preparing the effective polymer-retarding activators. By utilizing these aryloxy-aluminoxanes, the mass fraction of polymers in the total products could be reduced to lower than 1.0 wt%, which is much lower than that of the MAO-activated systems (> 30 wt%). This is a potential benefit for the industrial application of the iron-catalyzed oligomerization process.

Keywords Ethylene oligomerization; Bis(imino)pyridyl iron catalysts; Aryloxy-aluminoxanes; Phenols; Trimethylaluminum hydrolysis

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INTRODUCTION

Linear α -olefins are industrially highly desired compounds which are now mainly produced by the oligomerization of ethylene^[1]. Among the numerous catalysts for this reaction, bis(imino)pyridyl (BIP) iron catalysts with small mono-*ortho*-alkyls on the *N*-aryl rings have exhibited extremely high activity and selectivity to the target linear products^[2–5]. At present, methylaluminoxane (MAO) and modified methylaluminoxanes (MMAO) have been proved to be the most effective and used activators for the activation of these catalysts^[6–8]. However, barriers still remain to the commercial development of these systems with MAOs. Firstly, the use of large excesses of MAO leads to very high cost of the overall catalyst package^[9]. Secondly, the distribution of ethylene oligomers obtained from the MAO-activated systems is very broad; the proportion of undesired insoluble polymers can be higher than 30 wt% in the total products even the mono *ortho*-methyl substituted BIP-Fe complexes are employed^[10, 11]. Such mixtures can result in extensive reactor fouling and be hardly separated in the following product separation sections.

For the first problem, a commonly adopted solution is to immobilize the catalysts on silica or other supports^[12–15].

This may be helpful in reducing the activator dosage, but would increase the product molecular weight at the same time, which is unfavorable for the oligomerization process. For the second problem, a potential solution is to introduce electron-withdrawing groups into the ligand framework or extend the iron complexes with other tridentate models^[16–18]. Several BIP iron catalysts with fluorine atoms on the *ortho*-positions of the *N*-aryl rings were proved to trigger no ethylene to polymers^[19–23]. However, MAO continued to be the best activator for these systems. Since the nature of the activators would also largely affect the nature and the catalytic performance of the active species, as well as the final product properties, considerable efforts have also been devoted to modifying the activators or finding potential alternatives to MAO^[24, 25]. Compared to MAO, common alkylaluminum reagents AlR_3 ($\text{R} = \text{Me}, \text{Et}$ or *i*-Bu) are significantly lower in cost. Although they were proved to be effective activators for the iron-catalyzed ethylene polymerization^[26–34], none of them could be suitable in the oligomerization systems^[35, 36]. This may be due to the less bulky *ortho*-substituents in the oligomerization catalysts, which could not efficiently hinder the coordination of AlR_3 to form dormant alkyl-bridged species^[35], or to form paramagnetic LAlR_2 derivative *via* the transmetalation reactions involving transfer of the ligand from iron to aluminum^[37].

Concerning the specific iron-catalyzed oligomerization process, examples of alternative activators to MAO are

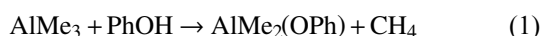
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scarce at present. Hanton *et al.*^[9] replaced MAO with AlEt₃ in combination with the perfluoro-borate or -aluminate [Ph₃C][B(Ph^F)₄] or [Ph₃C][Al(O^FBu^F)₄], but noticeable catalyst deactivation was observed. More recently, Boudier and co-workers^[36] discovered that the reaction products of phenol-, alcohol- and diol-derivatives with AlMe₃ could promote the iron-catalyzed ethylene oligomerization, but the activities remained much lower than the MAO-activated systems. It is now clear to us that an activator should be large enough and able to form the non-coordinating anion after activation, so that a stabilizing environment for the active species can be provided during the polymerization^[25]. That is why a number of alkylaluminoxanes (beyond MAO) obtained from the controlled hydrolysis of the corresponding trialkylaluminums or their mixtures could show good activities towards metallocene- or iron-catalyzed olefin polymerization^[38–44]. Therefore, our strategy for potential activator searching will focus on the MAO-like species in this work.

Recently, we proposed an effective strategy for retarding the simultaneous polymer formation during ethylene oligomerization by MAO modification with phenols^[45, 46]. It was found that phenols could readily react with AlMe₃ and the Al-Me moieties of MAO, leading to scavenging of AlMe₃ in MAO solution and phenoxy-decoration on MAO (Eqs. 1–3).



As also evidenced by Busico and co-workers^[47, 48], such effects would efficiently tune the composition of MAO, and further change its size, structure, Lewis acidity and reactivity. Most importantly, our results showed that the decoration of phenoxy groups would significantly reduce the product molecular weight and retard the polymer formation. It may lead to a better separation of the active cation-anion ion pairs, favoring the growing chain rotation and β -H transfer, finally shifting the product distribution towards lighter olefins. However, due to the existence of reactions (1) and (2), the true ratio between MAO and PhOH in the reaction shown in Eq. (3) is unknown. All of these findings encourage us to develop a series of aryloxy-aluminoxanes, directly from the hydrolysis of reaction products of AlMe₃ and phenols, which can be regarded as a thorough modification of MAO from its production. Such aryloxy-aluminoxanes may serve as a more effective generation of “polymer-retarding” activators, especially for the iron-catalyzed ethylene oligomerization, thus avoiding the use of MAO.

The idea for a possibility of producing aryloxy-aluminoxanes has been evidenced by the results of Kissin^[49, 50]. He found that the aluminoxanes bearing phenoxy groups with chemical or steric protection of both *ortho*-positions could serve as the activators for metallocene complexes, while *ortho*-unsubstituted ones could not be used for this purpose. No special attention was paid to the influence of aluminoxanes on the product molecular weight.

However, it was confirmed in our case that more efficient modifications on MAO could be achieved with *ortho*-unsubstituted phenols, and meanwhile the catalytic activities remained at a high level^[45]. Therefore, we prepared and tested the aryloxy-aluminoxanes, or named phenoxy-aluminoxanes, using the optimized *ortho*-unsubstituted phenols found in our previous work, and focused on the discussion about the impacts of [PhOH]/[AlMe₃] molar ratio and activator structure on the product distribution.

EXPERIMENTAL

Materials

All manipulations involving air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen glove-box. Solvents and reagents (toluene, *n*-heptane, *n*-butanol) were dried over 4 Å molecular sieves for at least 10 days. Toluene was then further purified by solvent purification system of Innovative Technology (PS-400-5-SD, USA). Iron(III) acetylacetonate (Fe(acac)₃, 99%), 2,6-diacetylpyridine (97%), 4-methoxy-2-methylaniline (98%) were purchased from J&K Chemical Corp. (Shanghai, China) and used without further purification. In the present work, PhOH represents the phenolic compounds, while C₆H₅OH represents the specific molecule of unsubstituted phenol. C₆H₅OH (98%), 4-*tert*-butylphenol (4-*t*-BuPhOH, 98%) and 4-bromophenol (4-BrPhOH, 99%) were purchased from TCI China (Shanghai, China). 2-Naphthol (2-NaPhOH, 99%) and cyclohexanol (98%) were purchased from J&K Chemical Corp. (Shanghai, China), and they were dried and dissolved in toluene (1.0 mol/L) prior to use. Deuterated 1,2-dichlorobenzene (C₆Cl₂D₄, 99.5 atom % D) was purchased from Sigma-Aldrich (Shanghai, China), freeze-pumped and transferred into a Schlenk bottle with activated 4 Å molecular sieves. Trimethylaluminum (AlMe₃, 2.0 mol/L in toluene) was purchased from Aladdin Biochemical Technology (Shanghai, China) and used as received. MAO (10 wt% solution in toluene) was purchased from Albermarle Chemical Corp. (Baton Rouge, LA, USA) and stored at –18 °C. High-purity nitrogen and polymerization-grade ethylene were obtained from SINOPEC Shanghai Corp. (Shanghai, China) and were passed through the oxygen- and moisture-scrubbing columns prior to use.

Preparation of the Catalyst Precursor

The ligand 2,6-bis[1-(4-methoxy-2-methylphenylimino)ethyl]pyridine (**L**, Fig. 1) used in this study was synthesized according to our previous work^[11]. It was then premixed with Fe(acac)₃ in toluene to form a homogeneous orange-red catalyst precursor (**L**:Fe(acac)₃ = 1:1, mol:mol), abbreviated as **L-Fe(acac)₃**. The concentration of the catalyst precursor in toluene, in terms of iron atoms [Fe], was 4 μmol/mL.

Procedure for *in situ* Preparation of Aryloxy-aluminoxanes

Aryloxy-aluminoxanes were prepared directly from the hydrolysis of reaction products of AlMe₃ and phenols *via* a two-step procedure in this work: (I) a reaction between AlMe₃ and phenol and, (II) a reaction between the products

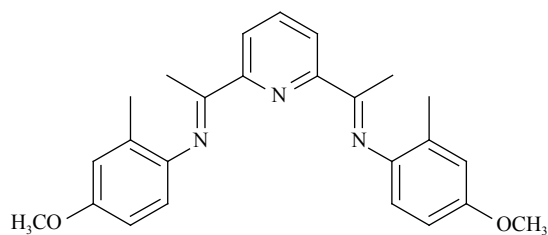


Fig. 1 Structure of 2,6-bis[1-(4-methoxy-2-methylphenylimino)ethyl]pyridine (L)

of the first step and water. A 250-mL glass reactor equipped with an ethylene inlet, vacuum line and magnetic stirrer was used. It was firstly heated by a heat gun for at least 15 min and purged with three cycles of nitrogen-vacuum. After cooling to 0 °C, 50 mL of toluene and 4.0 mmol of AlMe_3 were successively charged into the reactor. To such a solution was slowly added dropwise the phenols (or cyclohexanol). The mixture was allowed to react for 30 min under N_2 atmosphere for protection. An agitation speed around 700 r/min was employed. For the next step, the required amount of degassed distilled water was added slowly to the resultant product of the first step, which was then reacted for 15 min before increasing the temperature to 20 °C for another 15 min. Without further treatment, the activator mixture thus prepared was used in the iron-catalyzed oligomerization of ethylene.

Ethylene Oligomerization

To initiate the oligomerization, the temperature was further increased to 50 °C. Meanwhile, nitrogen was removed by a continuous flow of ethylene. The ethylene was allowed to exit *via* the oil-filled bubbler to maintain a constant 0.1 MPa of pressure over the reaction. After the injection of a solution of the catalyst precursor, the oligomerization was started. In the cases of AlMe_3 - or MAO-activated oligomerization, reaction was initiated after the addition of AlMe_3 or MAO, as well as the catalyst precursor. At the end of a run, the reaction was terminated by the addition of 3 mL of acidified ethanol and the reactor was cooled down to room temperature. The product mixture was then filtered to separate the oligomers in toluene and the insoluble polyethylene wax. The wax was washed sufficiently with toluene to drip down the light fraction in the filtrate, then washed with ethanol and dried under vacuum.

Characterization

The ^1H - and ^{27}Al -NMR spectra of the aluminum-based activators in a 5 mm sealed NMR tube were recorded at 600 and 156 MHz, respectively, using an Agilent 600 MHz DD2 (DirectDrive2) spectrometer at 25 °C. A mixture of toluene and 1,2-dichlorobenzene- d_4 was used as the solvent (0.2 mmol $_{[\text{Al}]}$ /mL). The catalytic activity was quantified by the amount of total products (oligomers and insoluble polymers). For oligomers, individual olefins were identified by GC/MS (Nicolet HP GC6890/MS5973). C_{12} olefin isomers were used to determine the selectivity to linear α -olefins. Further quantitative analyses were performed by Agilent GC 6890 equipped with a HP-5 column (5% phenylmethylsiloxane, 30 m $\times$ 0.32 mm $\times$ 0.25 μm) using *n*-

heptane as the internal standard. The injector temperature was 320 °C and the following temperature program was: 50 °C/2 min, 50–300 °C/(20 °C/min), 300 °C/10 min. Under this temperature programme, olefins ranging from C_4 to C_{34} can be detected. The yield of volatile C_4 fraction was determined by extrapolation of α value. The α value is a characteristic coefficient of Schulz-Flory distribution, which can be calculated from the relative rate of chain propagation and chain termination or the quotient of the molar amounts of two subsequent oligomer fractions, C_{14} and C_{12} in this case (Eq. 4).

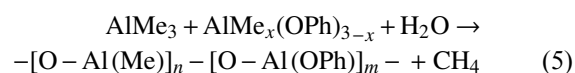
$$\alpha = \frac{\text{Rate of propagation}}{\text{Rate of propagation} + \text{Rate of termination}} = \frac{\text{mol}(\text{C}_{n+2})}{\text{mol}(\text{C}_n)} \quad (4)$$

RESULTS AND DISCUSSION

Aryloxy-aluminoxane Preparation and Catalyst Activation

It was found in our previous work^[45] that the *para*-alkyl or *para*-halogen substituted phenols with the *ortho*-positions unsubstituted served as effective MAO modifiers for the iron-catalyzed ethylene oligomerization. With the enlargement of *para*-alkyl size from methyl to *tert*-butyl or *para*-halogen from F to Br, the polymer share in the total products would be largely reduced. In particular, 4-BrPhOH was proved to be the most efficient polymer-retarding modifier among the studied phenols. Therefore, 4-BrPhOH was firstly employed for the preparation of the corresponding aryloxy-aluminoxanes.

It is clear that both the molar ratios of $[\text{PhOH}]/[\text{AlMe}_3]$ and $[\text{H}_2\text{O}]/[\text{Al}]$ would significantly affect the final structure, composition and reactivity of the obtained aluminoxanes. For the $[\text{PhOH}]/[\text{AlMe}_3]$ ratio, if it is up to 2.0, the most likely reaction between AlMe_3 and PhOH will be Eq. (2), and the main final reaction product after addition of water would be the dimer $(\text{PhO})_2\text{Al}-\text{O}-\text{Al}(\text{OPh})_2$ ^[50]. The polymerization degree of this product is too low to mimic the structure of MAO. Even when the ratio is decreased to 1.0 (resulting mostly in the reaction shown in Eq. 1), most of the methyl groups of $\text{AlMe}_2(\text{OPh})$ will be consumed in the following hydrolysis stage, leading to the formation of methyl-depleted aluminoxane, which is less effective in catalyst methylation^[45]. Therefore, the $[\text{PhOH}]/[\text{AlMe}_3]$ ratios in the present work will be controlled less than 1.0. Under such conditions, the plausible hydrolysis process can be expressed by Eq. (5).



where the aluminoxane products would contain two types of units, $-\text{Al}(\text{OPh})-\text{O}-$ and $-\text{Al}(\text{Me})-\text{O}-$. In contrast to the AlMe_3 hydrolysis at very low temperatures under carefully controlled conditions, the hydrolysis of the product obtained from the reaction between AlR_3 and phenol could be carried out under more moderate conditions^[49, 50]. In our study, the reaction between AlMe_3 and phenol was conducted at 0 °C and water was slowly added at the same

temperature. After 15 min from water addition, the temperature was slowly increased to 20 °C to continue the reaction. Oligomerizations were then initiated by the introduction of ethylene and the pre-catalyst **L-Fe(acac)₃** adapting the molar ratio of [Al]/[Fe] to be 2000 and routinely performed at a temperature of 50 °C over 30 min. The influence of [−OH]/[Al] and [H₂O]/[Al] molar ratios on ethylene oligomerization was systematically studied. The results are presented in Table 1.

To provide a baseline measure when the performance of phenoxy-aluminosiloxanes was examined, the oligomerizations activated by AlMe₃ and MAO were firstly tested under otherwise identical conditions. As expected, AlMe₃ was not a good activator for our BIP-Fe complex; the activity of **L-Fe(acac)₃/AlMe₃** was very low, affording only few C₄ and C₆ oligomers (Entries 1 and 2, Table 1). When MAO was employed as the activator, the activity was as high as 6140 kg/(mol_{Fe}·h), and a large amount of insoluble polymers (36.8 wt%) was produced (Entry 3). We also tried to make the “MAO” from AlMe₃ hydrolysis under our conditions with [H₂O]/[Al] = 0.7. The catalytic result showed that the activity of this self-made MAO was even higher than the commercial MAO, achieving 13050 kg/(mol_{Fe}·h) (Entry 10). Meanwhile, the mass fraction of polymers in the total products, 52.3 wt%, was also higher than that of the commercial MAO. Since the AlMe₃ hydrolysis reaction is fast and highly exothermic, we tentatively attribute it to the relatively higher hydrolysis temperature in this work, which may make the self-made MAO bigger in size (higher polymerization degree) and more irregular in structure than the commercial one, thus increasing its Lewis acidity and activity^[51, 52], and imposing greater steric hindrance on the active species favoring the formation of higher molecular

weight products^[45].

The phenoxy-aluminosiloxanes prepared with different [−OH]/[Al] and [H₂O]/[Al] molar ratios were then tested. As evidenced in Table 1, these aluminosiloxane activators bearing 4-Brphenoxy groups are very active towards iron-catalyzed ethylene oligomerization; the activities are comparable to or even higher than the commercial MAO-activated system, especially at a low [−OH]/[Al] ratio. Most importantly, when the [−OH]/[Al] ratio is higher than 0.3, the oligomerization products contain much less polymers (< 7.0 wt%), indicative of the significant polymer-retarding effect of these activators. For better understanding, the influence of [−OH]/[Al] and [H₂O]/[Al] ratios on the catalytic performance is more clearly illustrated in Fig. 2. During the hydrolysis process, three [H₂O]/[Al] molar ratios, 0.5, 0.7 and 0.9, were employed. It can be seen that the [H₂O]/[Al] ratio affects both the activity and polymer production. Although high activities and low polymer yields could be observed under different [H₂O]/[Al] ratios, higher activities and fewer polymers were obtained when [H₂O]/[Al] = 0.7. This value was proved to be more ideal for the formation of effective polymer-retarding activators. At the same time, the activity and polymer production were largely affected by the [−OH]/[Al] ratio. With the [−OH]/[Al] ratio increased from 0.3 to 0.9, the activity decreased remarkably (Fig. 2a). There are two factors which might explain this observation. One is that more −OPh groups will replace the −Me groups on the resultant aluminosiloxane with the increase of [−OH]/[Al] ratio, thus lowering the methylation ability of the activator. The other is that there might be a hydrolysis occurring at the Al−OPh bond to release the corresponding phenols^[53–55]. Although this re-generated 4-Brphenol will continue reacting with the

Table 1 Oligomerizations activated by the reaction products of 4-BrPhOH, AlMe₃ and water ^a

Entry	[−OH]/[Al] (mol/mol)	[H ₂ O]/[Al] (mol/mol)	Oligomer			Polymer		Activity ^f
			<i>Y_o</i> ^b (g)	<i>α</i>	LAO content ^c (%)	<i>Y_p</i> ^d (g)	PE content ^e (wt%)	
1 ^g	–	–	0.10	–	96	0	0	100
2 ^h	–	–	0.06	–	99	0	0	60
3 ⁱ	–	–	3.88	0.73	97	2.26	36.8	6140
4	0.30	0.50	5.07	0.69	96	0.35	6.5	5420
5	0.40	0.50	4.10	0.69	97	0.18	4.2	4280
6	0.50	0.50	3.76	0.69	97	0.10	2.6	3860
7	0.60	0.50	1.19	0.70	98	0.02	1.7	1210
8	0.70	0.50	0.64	0.68	98	Trace	–	640
9	0.90	0.50	0.13	0.68	98	Trace	–	130
10	–	0.70	6.22	0.76	96	6.83	52.3	13050
11	0.10	0.70	5.84	0.77	96	5.68	49.3	11520
12	0.30	0.70	5.70	0.69	97	0.15	2.6	5850
13	0.40	0.70	5.06	0.68	97	0.19	3.6	5250
14	0.50	0.70	3.48	0.69	98	0.03	0.9	3510
15	0.70	0.70	1.00	0.68	98	0.01	1.0	1010
16	0.90	0.70	0.55	0.70	98	Trace	–	550
17	0.30	0.90	4.18	0.70	99	0.31	6.9	4490
18	0.50	0.90	2.50	0.69	99	0.10	3.8	2600
19	0.70	0.90	0.84	0.69	99	0.006	0.7	846
20	0.90	0.90	0.27	0.69	99	Trace	–	270

^a General conditions: pre-cat.: **L-Fe(acac)₃**, [Fe] = 2 μmol; [Al]/[Fe] = 2000; solvent: toluene, 50 mL; *T* = 50 °C; *P* = 0.1 MPa; *t* = 30 min; ^b Yield of the soluble oligomers, determined by GC; ^c Linear *α*-olefin content (%) in oligomers determined by GC; ^d Yield of the insoluble polymers; ^e The mass fraction of insoluble polymers in the total products (soluble oligomers + insoluble polymers); ^f Total activity: kg/(mol_{Fe}·h); ^g AlMe₃ as co-catalyst, [Al]/[Fe] = 500; ^h AlMe₃ as co-catalyst, [Al]/[Fe] = 2000; ⁱ MAO as co-catalyst, [Al]/[Fe] = 2000.

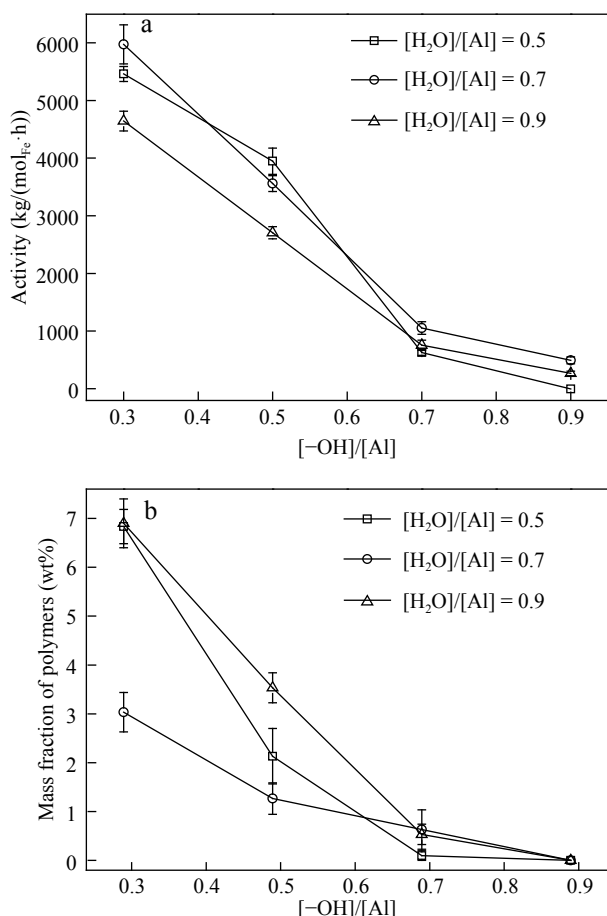


Fig. 2 Influence of $[-OH]/[Al]$ and $[H_2O]/[Al]$ molar ratios on the catalytic activity (a) and polymer production (b)

resultant aluminosilicate, there is an increasing possibility for it to poison the active species as the initial dosage increases.

Concerning the polymer production, it can be seen from Table 1 and Fig. 2(b) that with the $[-OH]/[Al]$ molar ratio increased from 0.1 to 0.9, the mass fraction of insoluble polymers in the total products was greatly decreased. For the systems activated by commercial MAO, self-made MAO or the phenoxy-aluminosilicate prepared with $[-OH]/[Al] = 0.1$ (Entries 3, 10 and 11, Table 1), the insoluble polymers accounted for nearly half of the total products, making the mixture a slurry, which would be a big trouble for reaction, product transportation and separation procedures. However, when we used the phenoxy-aluminosilicate prepared with $[-OH]/[Al]$ ratio up to 0.5, the polymer share could be reduced to lower than 4.0 wt%, leading to a nearly clear olefin solution. Meanwhile, a reduction of the Schulz-Flory α value could be observed. Based on our previous work^[45] and a recent report on the pentafluorophenyl- or pentafluorophenoxy-modified solid polymethylaluminosilicates^[56], it was deduced that the $-OPh$ groups on the activator surface would facilitate a better separation of the active ion pairs, which might promote the coordination of ethylene monomer. Although this would be beneficial for the monomer insertion, the β -H transfer would be accelerated at the same time, since the bimolecular β -H transfer to monomer reaction has been proposed as the main termination process for the BIP-iron

systems^[57]. In addition, a larger ion-pair separation would reduce the steric hindrance on the active species, which would further lower the energy barriers for an attractive Fe-H interaction and the β -H transfer, thus shift the product distribution towards lower molecular weight and retard the formation of polymers.

To balance the impacts of $[-OH]/[Al]$ on activity and polymer production, an optimized value of this ratio is ~ 0.5 , under which the potential alternatives to MAO can be obtained with good polymer-retarding effect and relatively high activity. Fig. 3 shows the typical olefin distributions resulting from the systems activated by the phenoxy-aluminosilicates prepared with $[-OH]/[Al] = 0.5$. The distributions follow the Schulz-Flory rules with the characteristic coefficient α to be 0.69, which is quite desired for the industrial production of α -olefins.

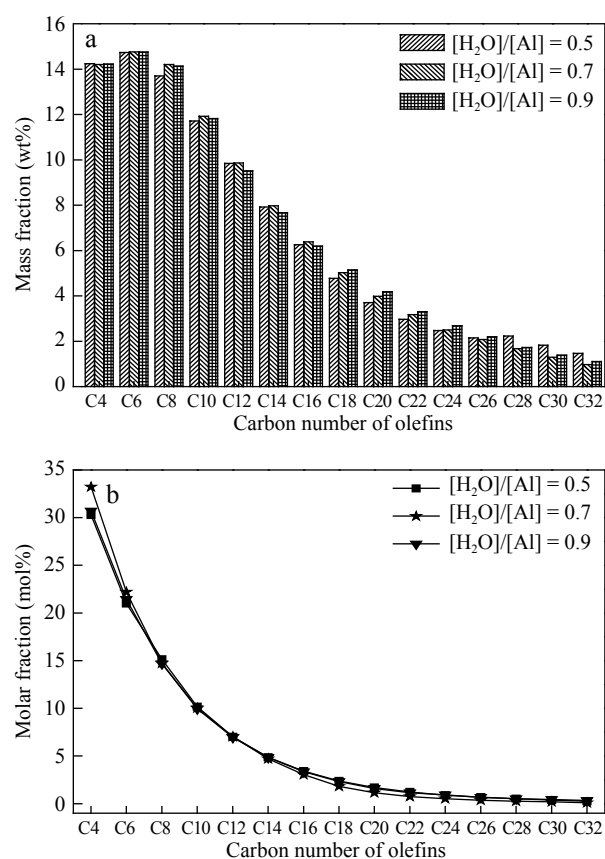


Fig. 3 Typical weight distributions (a) and molar distributions (b) of olefins obtained from various 4-Brphenoxy-aluminosilicate-activated systems with $[-OH]/[Al] = 0.5$ (Entries 6, 14 and 18, Table 1)

NMR Analysis of the Aluminosilicate Activators

It is generally accepted that the alkylaluminosilicates are a mixture of oligomeric clusters with three-dimensional cage-like structures^[58]. Although they are complex mixtures, spectroscopic analyses can be attempted to gain a better understanding of their structural information. Therefore, the reaction product of 4-BrPhOH, $AlMe_3$ and water prepared under the optimized conditions ($[-OH]/[Al] = 0.5$, $[H_2O]/[Al] = 0.7$) was chosen to be further studied using the

^1H - and ^{27}Al -NMR analyses. Signal of methyl protons of toluene (2.16 ppm) in $\text{C}_6\text{Cl}_2\text{D}_4$ was used as the internal reference for the ^1H -NMR spectrum. Fig. 4 shows that this product has a broad signal at approximately $\delta_{\text{H}} = -1.0$ ppm to 0.1 ppm with four sharp peaks at $\delta_{\text{H}} = -0.67$, -0.44 , 0.17 and 0.24 ppm in the hydride region of the ^1H -NMR spectrum. According to the assignment of the ^1H -NMR spectrum of MAO in several publications^[47, 59–62], the broad signal could be ascribed to the polymeric aluminoxane structure, indicating the formation of MAO-like products in our work. Concerning the sharp peaks, the singlet resonance at $\delta_{\text{H}} = 0.17$ ppm should correspond to methane (CH_4), which is a side-product of the reactions. The resonance at $\delta_{\text{H}} = -0.44$ ppm may be ascribed to the unreacted AlMe_3 , while the other two peaks at $\delta_{\text{H}} = -0.67$ and 0.24 ppm may belong to the terminal $\text{Al}-\text{Me}$ and bridged $\text{Al}-\text{Me}-\text{Al}$ protons, respectively, probably from the mono- or dinuclear phenoxyalkylaluminums^[45, 53, 54, 63]. The integration ratios of the sharp peaks with respect to the broad signal were 2.8% ($\delta_{\text{H}} = -0.67$ ppm), 2.2% ($\delta_{\text{H}} = -0.44$ ppm) and 7.3% ($\delta_{\text{H}} = 0.24$ ppm), showing that the total content of these aluminum species in the aluminoxane product was *ca.* 12.3%.

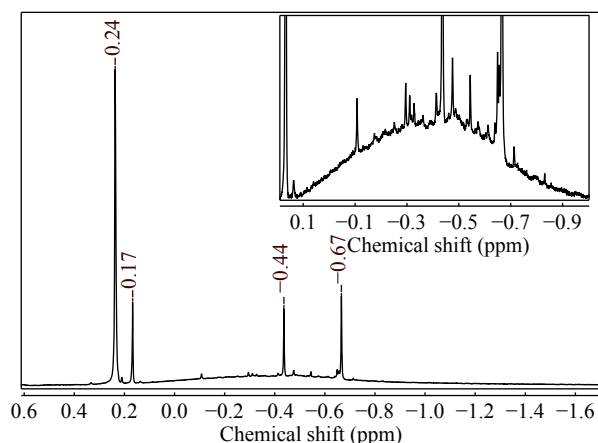


Fig. 4 Fragments of ^1H -NMR spectrum of the 4-Brphenoxy-aluminoxane prepared with $[-\text{OH}]/[\text{Al}] = 0.5$ and $[\text{H}_2\text{O}]/[\text{Al}] = 0.7$ (600 MHz, ODCB-d_4)

Fig. 5 shows the ^{27}Al -NMR spectra of AlMe_3 , commercial MAO, 4-BrPhOH-modified MAO and 4-Brphenoxy-aluminoxane. It can be seen that the ^{27}Al -NMR spectrum of pure AlMe_3 consists of a single signal at $\delta_{\text{Al}} = 154$ ppm and a background signal centered at 50 ppm. For comparison, the ^{27}Al -NMR spectrum of commercial MAO has two peaks at $\delta_{\text{Al}} = 159$ and 60 ppm, respectively. According to the assignment of the ^{27}Al -NMR spectrum of MAO in the literatures^[59, 64, 65], the resonance at $\delta_{\text{Al}} = 159$ ppm can be assigned to part of the Al environment in MAO, which most likely coincides with the signal of AlMe_3 present in the MAO sample. The peak at $\delta_{\text{Al}} = 60$ ppm could be a merged one; apart from the background signal, there should exist some other Al resonance, which may belong to MAO itself^[59]. With the addition of 4-BrPhOH into the MAO sample, the peak at $\delta_{\text{Al}} = 159$ ppm disappears, leaving the only one peak located at $\delta_{\text{Al}} = 61$ ppm. As aforementioned,

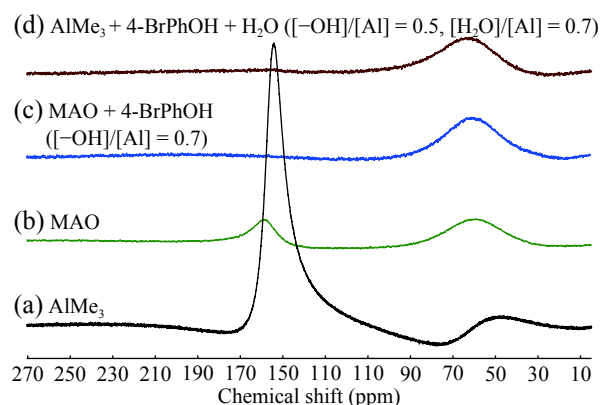


Fig. 5 ^{27}Al -NMR spectra of AlMe_3 (a), MAO (b), 4-BrPhOH-modified MAO (c) and the 4-Brphenoxy-aluminoxane (d) (156 MHz, ODCB-d_4)

the addition of phenols into MAO will scavenge the free AlMe_3 , leading to the formation of aluminum phenoxides $\text{AlMe}_x(\text{OPh})_{3-x}$. Here, the chemical environment for Al atom in $\text{AlMe}(\text{OPh})_2$ is $-\text{OAl}(\text{Me})\text{O}-$, and the $\text{AlMe}_2(\text{OPh})$ may form a dinuclear compound with exclusively phenoxide bridged^[54]. The ^{27}Al -NMR resonances for these compounds were tentatively proposed to be similar with that of MAO at around 60 ppm. Our reaction product of 4-BrPhOH, AlMe_3 and water also shows a single broad signal at approximately 60 ppm (centered at $\delta_{\text{Al}} = 64$ ppm), which again confirms the formation of aluminoxane structures. All these results indicate that 4-BrPhOH is involved in the hydrolysis of AlMe_3 and the aryloxy groups change the chemical environment of Al atoms, leading to the reduction of insoluble polymers and high activity of the catalytic systems.

AlMe_3 Hydrolysis in the Presence of Other Phenols

To further verify the activation effectiveness of the aryloxy-aluminoxanes for iron-catalyzed ethylene oligomerization, unsubstituted phenol ($\text{C}_6\text{H}_5\text{OH}$) and *para*-alkyl substituted phenol (4-*t*-BuPhOH) were also employed to prepare the corresponding phenoxy-aluminoxanes. Hereby, the $[\text{H}_2\text{O}]/[\text{Al}]$ molar ratio used in the hydrolysis procedure was fixed at 0.7. As shown in Table 2, these aluminoxanes also serve as highly effective activators; the activities and the polymer-retarding abilities are close to those of the 4-Brphenoxy-aluminoxanes. As expected, the $[-\text{OH}]/[\text{Al}]$ molar ratio adopted in the first step of reaction with AlMe_3 has very significant impacts on the catalytic activity, olefin distribution, and most importantly the polymer formation. There is a sharp reduction of the polymer yields as the $[-\text{OH}]/[\text{Al}]$ ratio increases from 0.1 to 0.7. In these cases, $[-\text{OH}]/[\text{Al}] = 0.5$ continues to be the optimized value, which can largely retard the polymer production and maintain the activity at a high level.

Noteworthy, if we make a comparison of the polymer-retarding performance between the activators shown in Table 2 and the MAOs modified by the corresponding phenols in our previous work^[45], it can be found that the phenoxy-aluminoxanes here perform much better than the phenol-modified MAOs under the same $[-\text{OH}]/[\text{Al}]$ ratio. For examples, when $[-\text{OH}]/[\text{Al}] = 0.3$ and 0.5 , the polymer

Table 2 Oligomerizations activated by the reaction products of C₆H₅OH/4-*t*-BuPhOH, AlMe₃ and water ^a

Entry	[−OH]/[Al] (mol/mol)	[H ₂ O]/[Al] (mol/mol)	Oligomer			Polymer		Activity ^c
			Y _o (g)	α	LAO content (%)	Y _p (g)	PE content ^b (wt%)	
[−OH]: C ₆ H ₅ OH								
21	0.10	0.70	5.47	0.75	97	4.19	43.4	9660
22	0.30	0.70	4.65	0.68	98	0.17	3.5	4820
23	0.50	0.70	2.52	0.68	99	0.03	1.2	2550
24	0.70	0.70	1.18	0.70	99	0.01	0.8	1190
25	0.90	0.70	0.29	0.68	98	Trace	–	290
[−OH]: 4- <i>t</i> -BuPhOH								
26	0.10	0.70	6.64	0.76	96	5.20	43.9	11840
27	0.30	0.70	5.53	0.68	97	0.48	8.0	6010
28	0.50	0.70	2.41	0.69	99	0.04	1.6	2450
29	0.70	0.70	1.34	0.68	99	0.01	0.7	1350
30	0.90	0.70	0.30	0.68	97	Trace	–	300

^a General conditions: pre-cat.: L-Fe(acac)₃, [Fe] = 2 μmol; [Al]/[Fe] = 2000; solvent: toluene, 50 mL; T = 50 °C; P = 0.1 MPa; t = 30 min; ^b The mass fraction of insoluble polymers in the total products; ^c Total activity: kg/(molFe·h)

share of the 4-*t*-BuPhOH-modified MAO activated systems is 18.9 wt% and 6.5 wt%, respectively, which are obviously higher than the values of Entries 27 and 28 in Table 2. Such a difference in polymer yields is even greater when the same amount of C₆H₅OH is used to modify MAO or to prepare the phenoxy-aluminosiloxanes. As mentioned above, the true ratio between MAO and PhOH is influenced by the amount of free AlMe₃. Since part of the phenols are consumed in the reaction with AlMe₃, more phenols will be needed to interact with the true MAO. However, in the direct hydrolysis of AlMe₃ and PhOH, more −OPh groups could be incorporated and well distributed into the aluminosiloxane backbone. A better polymer-retarding effect can therefore be achieved even with a lower initial dosage of phenols.

The weight distributions of oligomers obtained with the activation of the C₆H₅O-aluminosiloxanes and 4-*t*-Buphenoxo-aluminosiloxanes are shown in Figs. 6 and 7, respectively. It can be found that the increase of [−OH]/[Al] ratio in these activator syntheses also leads to the gradual shift of distribution towards lighter olefins, again verifying that the β-H transfer is promoted with the increase of [−OH]/[Al] ratio.

AlMe₃ Hydrolysis in the Presence of PhOH-like Modifiers

Besides the utilization of PhOHs as the [−OH] source in the

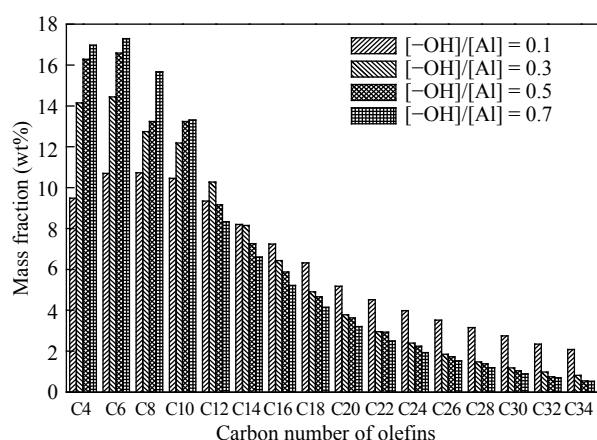


Fig. 6 Olefin distributions obtained from various C₆H₅O-aluminosiloxane-activated systems with [H₂O]/[Al] = 0.7

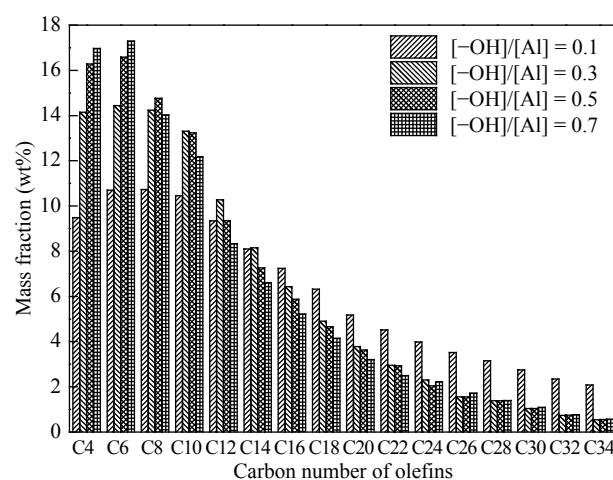


Fig. 7 Olefin distributions obtained from various 4-*t*-Buphenoxo-aluminosiloxane-activated systems with [H₂O]/[Al] = 0.7

first step of reaction with AlMe₃, two other types of [−OH], 2-naphthol and cyclohexanol, were also explored for the preparation of aluminosiloxane activators. The preparation conditions were identical to the aforementioned ones with the [H₂O]/[Al] ratio used in the hydrolysis procedure to be 0.7. The results are summarized in Table 3.

The naphthols are naphthalene homologues of phenol, with the hydroxyl group being more reactive. Therefore, when 2-naphthol was introduced into the AlMe₃ solution, it could readily react with AlMe₃ to form the corresponding aluminum aryloxides. After the addition of water, the aluminosiloxanes with NaphO-groups could be formed. As shown in Table 3, these activators exhibited high activities towards ethylene oligomerization. Particularly, when the [−OH]/[Al] ratio was 0.1, the activity was as high as 14970 kg/(molFe·h). However, the activity seemed to be more sensitive to the [−OH]/[Al] ratio in this case; a significant deactivation could be observed as the [−OH]/[Al] ratio increased. When the [−OH]/[Al] ratio was up to 0.7, it was almost inactive. This may be due to the more reactive nature of the hydroxyl group and the relatively bigger naphthalene ring in 2-naphthol. The former factor may lead to an overreaction with AlMe₃, and the latter one

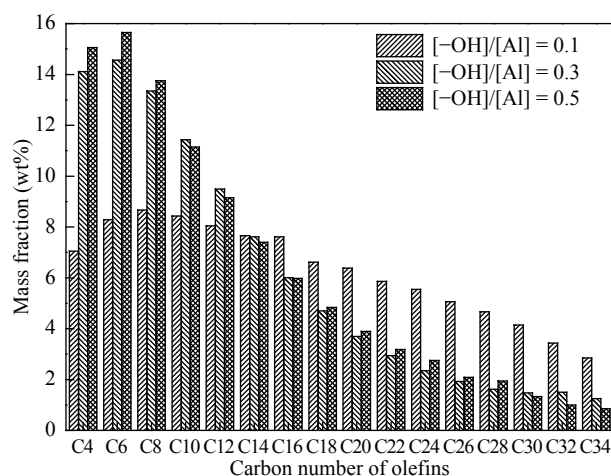
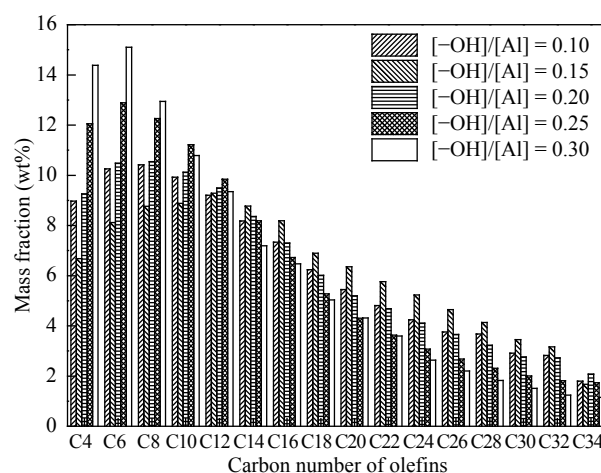
Table 3 Oligomerizations activated by the reaction products of 2-NaphOH/cyclohexanol, AlMe₃ and water ^a

Entry	[−OH]/[Al] (mol/mol)	[H ₂ O]/[Al] (mol/mol)	Oligomer			Polymer		Activity ^c
			Y _o (g)	α	LAO content (%)	Y _p (g)	PE content ^b (wt%)	
[−OH]: 2-NaphOH								
31	0.10	0.70	6.35	0.78	95	8.62	57.6	14970
32	0.30	0.70	4.60	0.69	98	0.23	4.8	4830
33	0.50	0.70	1.21	0.69	99	0.01	0.8	1220
34	0.70	0.70	–	–	–	–	–	–
[−OH]: Cyclohexanol								
35	0.10	0.70	4.04	0.76	96	4.48	52.6	8520
36	0.15	0.70	4.06	0.81	95	7.52	64.9	11580
37	0.20	0.70	4.99	0.75	97	4.22	45.8	9210
38	0.25	0.70	4.70	0.71	97	1.58	25.2	6280
39	0.30	0.70	0.07	0.66	92	Trace	–	70
40	0.50	0.70	–	–	–	–	–	–

^a General conditions: pre-cat.: L-Fe(acac)₃, [Fe] = 2 μmol; [Al]/[Fe] = 2000; solvent: toluene, 50 mL; T = 50 °C; P = 0.1 MPa; t = 30 min; ^b The mass fraction of insoluble polymers in the total products; ^c Total activity: kg/(mol_{Fe}·h)

may shield the methyl groups on the aluminoxanes and prevent them from getting close to the active species. Anyway, the aryloxy-aluminoxanes originated from the reactions between 2-NaphOH, AlMe₃ and water were still proved to be effective polymer-retarding activators. The mass fraction of polymers in the total products could be largely reduced to as low as 0.8 wt% when the [−OH]/[Al] ratio was 0.5. In addition, the olefin distributions followed the similar trend as afore-mentioned (Fig. 8).

A structurally similar and low toxic candidate compound, cyclohexanol, was also explored in this work. However, the activity showed very high sensitivity to the amount of cyclohexanol. High activities could only be obtained when the [−OH]/[Al] ratio was lower than 0.25. A slight increase of this ratio to 0.3 would largely deactivate the catalyst. The polymer yields, at the same time, remained very high (> 25 wt%) under the [−OH]/[Al] ratios from 0.1 to 0.25, although a slight reduction was observed. Moreover, Fig. 9 shows that the change of the resultant olefin distributions with the increase of [−OH]/[Al] ratio is much less significant in this case than the other systems. These results prove that cyclohexanol is not a suitable [−OH] candidate for the preparation of effective polymer-retarding activators.

**Fig. 8** Olefin distributions obtained from various 2-NaphO-aluminoxane-activated systems with [H₂O]/[Al] = 0.7**Fig. 9** Olefin distributions obtained from various cyclohexanol-modified-aluminoxane-activated systems with [H₂O]/[Al] = 0.7

Our findings, to some extent, confirm the importance of using phenols for the preparation of aluminoxane activators with good polymer-retarding effects and relatively high activities.

CONCLUSIONS

The simultaneous production of undesired polymers during the ethylene oligomerization is a big obstacle for the further commercialization of the bis(imino)pyridyl iron catalysts. In order to reduce such insoluble polymers, a series of aryloxy-aluminoxanes was prepared through the hydrolysis of the reaction products of AlMe₃ and phenols under different molar ratios of [PhOH]/[AlMe₃] and [H₂O]/[Al]. When applied to the iron-catalyzed oligomerization of ethylene, these aryloxy-aluminoxanes were proved to be highly active polymer-retarding activators. With the [PhOH]/[AlMe₃] ratio increased from 0.1 to 0.7, the polymer yields decreased remarkably, and a relatively clear olefin solution could be obtained. By comparing the catalytic performance of various aluminoxanes prepared with different phenols, 2-naphthol and cyclohexanol as [−OH] sources, the importance of using phenols was confirmed. The aryloxy-aluminoxanes

studied in this work can serve as potential alternatives to MAO, and their polymer-retarding effect is promising for the industrial application of the iron-catalyzed ethylene oligomerization process. The research on the relationship between the activator structure and their performance is now in progress. We are quite interested in the roles of aryloxy-decoration on aluminoxanes in retarding polymer formation during the ethylene oligomerization.

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