Routes to Reduce Aluminium Co-catalyst Content for Zirconocene Activation in Olefin Polymerization

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Summary : In this paper, we investigate different routes to lower drastically the amount of methylaluminoxane (MAO) required to activate racEt(Ind)$_2$ZrX$_2$ catalysts towards olefin polymerization. A first approach consists in replacing Cl ligands by more easily extractable X groups such as Me, CH_2Ph or NMe_2 groups. A second method focuses on the preparation of TMA-depleted MAO either by pumping off TMA from commercial MAO or by exploring new synthetic source to MAO via non-hydrolytic processes such as the reaction of TMA with benzophenone. Both methods allowed us to produce polyolefins with a maximal catalytic activity for Al/Zr ratios not exceeding 150, i.e. ratio 20 times lower than those required in the presence of commercial MAO.

Introduction

Although the discovery of metallocene-based catalytic systems twenty years ago was a real breakthrough in the field of olefin polymerization, the actual production of polyethylene (PE) and isotactic polypropylene (iPP) by this catalysis does not even exceed 5% of the world production. To compete with the last generation of supported conventional Ziegler-Natta catalysts which are highly active towards olefin polymerization and may also yield highly stereoregular polyolefins, metallocenes have obviously to be supported and activated efficiently at a low cost. Therefore, the development of metallocenes as olefin polymerization catalysts at an industrial scale requires to lower drastically the content of costly aluminium-based co-catalyst such as methylaluminoxane (MAO).

MAO is generally prepared by the partial hydrolysis of trimethylaluminium (TMA) in the presence of hydrated salts such as $Al_2(SO_4)_3$ 16 H_2O, ice or water vapour[1]. Not only the reaction between TMA and water requires stringent experimental conditions that explain the high cost for MAO but, in addition, the latter must be used in very large excess (Al/Met > 3000) to activate effectively di-chlorinated metallocenes. For all these reasons, it is particularly needed to explore new routes allowing to reduce

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the Al/Zr ratio while maintaining an optimal catalytic activity for olefin polymerization. In this regard, we investigated several routes to achieve this objective.

Results and discussion

Even if the MAO structure is not completely elucidated yet, the activation of L_2MetX_2 metallocenes by MAO is now well understood. By means of UV/visible spectroscopy[2], we could discriminate different elementary steps (a mono-methylation followed by a cationization) in the activation process of racEt(Ind)$_2$ZrX$_2$ by MAO.

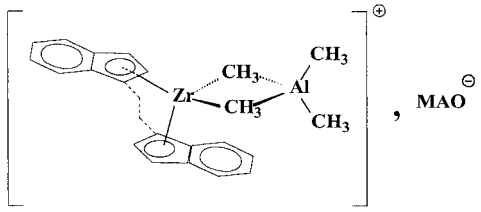
1/ Influence of the zirconocene extractable X ligand nature :

The nature of the abstracted X ligand was found to be a critical parameter in the zirconocene activation process. Indeed, abstraction of common Cl ligand from racEt(Ind)$_2$ZrCl$_2$ by MAO yields [MAO-Cl]$^-$ counter anions that strongly interacts with the zirconocene coordinating vacant site and impedes olefin polymerization[3]. This behavior explains why large amount of MAO is required (Al/Zr > 2000) to activate the metallocene and thus permit olefin polymerization. Unlike racEt(Ind)$_2$ZrCl$_2$/MAO catalytic system, the activation by MAO of racEt(Ind)$_2$ZrX$_2$ where X = Me, N(Me)$_2$ or CH_2Ph groups occurs at low Al/Zr ratios[4]. The influence of the nature of extractable X ligands on activation as well as on 1-hexene polymerization activity was checked. Data are gathered in Table 1.

Ligand X	Al/Zr molar ratio	λ_{max} (nm)	Activity Kg PH.molZr^{-1}.h^{-1}
Cl	150	440	0
	2000	470	1290
Me	150	439	1150
	2000	470	1190
NMe_2	40	435	27
	2000	470	30
CH_2Ph	50	432	940
	2000	470	970

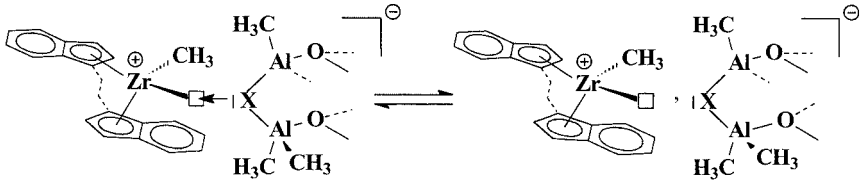
Table 1 : Influence of extractable X ligands onto racEt(Ind)$_2$ZrX$_2$ activation by MAO and hex-1-ene polymerization activity in toluene at 20°C, [hex-1-ene] = 1 mol.L^{-1}

As may be seen in Table 1, species obtained at high Al/Zr ratios (Al/Zr = 2000) have an absorption band located at 470 nm, whatever the nature of the zirconocene precursor. On the grounds of previous works made in our laboratory as well as literature data, a hetero bimetallic complex between zirconium and aluminium from TMA, as shown in Scheme 1, is postulated for such a species.



Scheme 1 : Hetero bimetallic species obtained at high Al/Zr ratios with an absorption band at 470 nm

Data given in Table 1 also demonstrate that "intermediate species" obtained at lower Al/Zr ratios (Al/Zr = 40-150) present an absorption band in the range 430-440 nm, depending on the X ligand nature. As already discussed, such a species is completely inactive towards hex-1-ene polymerization in the specific case of zirconocene bearing Cl ligand. Hypothetical structures of species absorbing in the range 430-440 nm is shown in Scheme 2. It highlights the possible coordination of the MAO-trapped X ligand onto zirconocenium active site in competition with the monomer coordination/insertion. The strength of the interaction between X and the vacant site of the metal center is very much dependent of the X electronic donating capacity.



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Scheme 2 : Hypothetical structures of species absorbing at 430-440 nm according to X nature (X = Cl, Me, NMe_2, CH_2Ph)

This shows that Cl ligand has a negative effect in the whole activation process of zirconocene by commercial MAO. The Cl substitution by more easily extractable and less coordinating X ligand enables to lower drastically the amount of MAO required to

activate effectively the zirconocene towards olefin polymerization.

2/ New synthetic routes to methylaluminoxane

2.1/ TMA-depleted MAO

Commercial MAO has a very complex structure with 30 wt% of residual TMA left. The role of TMA in commercial MAO for zirconocene activation towards olefin polymerization has been a pending question for long. TMA-depleted MAO was prepared to check the ability of the aluminoxane derivative alone (MAO*) to activate zirconocene catalysts. For that purpose, TMA was pumped off under vacuum at 80°C for several hours. The ^{1}H NMR spectra of both commercial MAO and MAO* are shown in Figure 1 ; the peak assigned to free TMA at –0,38 ppm has nearly vanished in MAO*.

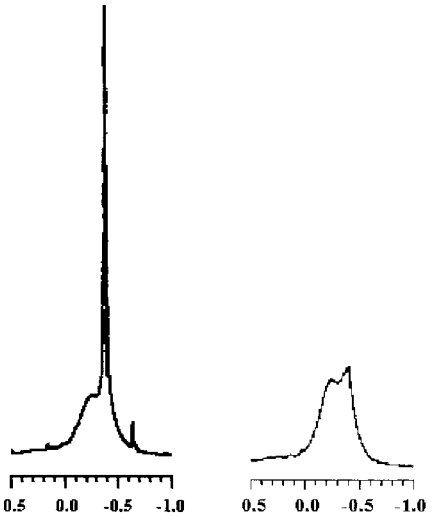


Figure 1 : ^{1}H NMR spectrum in toluene d^8 of commercial MAO (left) and MAO* (right) after heating treatment at 80°C under vacuum for several hours

Activation of racEt(Ind)$_2$ZrCl$_2$ by MAO* was investigated by means of UV/visible spectroscopy correlated to olefin polymerization kinetics[5]. MAO* was found to be a much powerful activator than commercial MAO. Indeed, addition of MAO* up to Al/Zr = 150 leads to the formation of species with an absorption band at 440 nm that revealed highly active towards hex-1-ene and ethylene polymerization. Activity values (1,1 Kg PHex/mol Zr.h and 4000 Kg PE/mol.Zr.h) were found similar to

those obtained with commercial MAO at very high Al/Zr ratios (2000-4000). This study stresses the drastic effect of MAO structure change onto the ability of MAO to activate zirconocenes. These experiments also indicate that remaining TMA may have a poisoning role in the activation process of metallocene dichloride. Our investigations, as well as literature data,[6] point out that TMA (free or condensed with MAO) may react with chlorinated zirconocene to form *in situ* $AlMe_2Cl$ – bonded or not to the MAO cage – that may strongly interacts with the metal center vacant site through the chlorine (see Scheme 2) and impedes olefin coordination and insertion. As a conclusion, it may be stressed that the combined presence of TMA and metallocenes with Cl ligands has to be avoided to obtain efficient catalytic systems towards olefin polymerization at low Al/Zr ratios.

2.2/ MAO from non-hydrolytic process

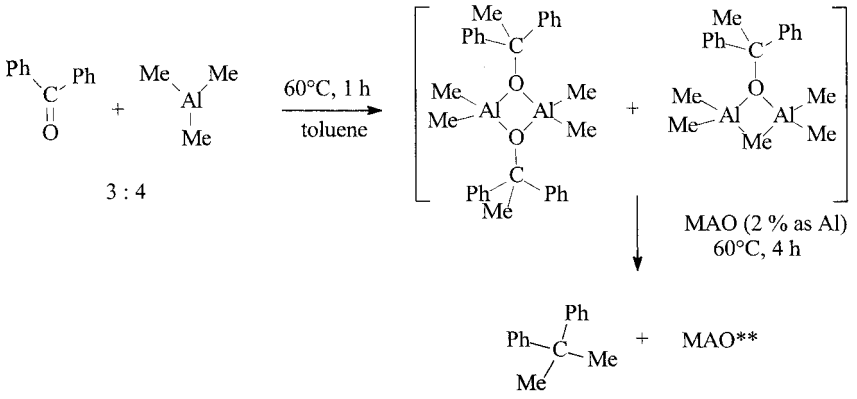
The reaction of TMA with ketones is described in the literature to yield various aluminoxane-type derivatives[7]. Depending on the initial ketone/TMA ratio and in the presence of catalytic amount of commercial MAO, some of the aluminium-based reaction products were found able in very specific conditions to activate zirconocenes[8].

In this study, the reaction between benzophenone and TMA was studied in details in toluene at 60°C using benzophenone/TMA ratios ranging from 1/1,09 to 1/1,8. The addition of catalytic amount of commercial MAO (2% with respect to Al from TMA) and further heating the solution at 60°C for 4 hours was found necessary to yield efficient MAO-type activator (MAO**) along with 2,2-diphenyl propane. On these grounds, a description of the reaction is proposed in Scheme 3.

The ability of MAO** to activate $racEt(Ind)_2ZrCl_2$ towards ethylene polymerization was further investigated according to the initial benzophenone/TMA ratio used. Data are gathered in Table 2. As may be observed, very high catalytic activity (twice the maximal value obtained in the presence of commercial MAO) is obtained when 1/1,3 ratio is used for the preparation of MAO**. It is also worth noting that the molar mass and molar mass distribution (MMD) of the polyethylene formed are similar to those obtained with commercial MAO as an activator.

Further increase or decrease of the benzophenone/TMA ratio rapidly lowers the catalytic activity. The chemical reasons (nature of the products formed) why the

catalytic activity towards olefin polymerization is very sensitive to the benzophenone/TMA ratio are currently under investigation [9].



Scheme 3 : Heating treatment of benzophenone with TMA followed by catalytic addition of commercial MAO to yield new MAO-type activator

Cocatalyst MAO** Benzophenone/TMA	Activity Kg PE/mol.Zr.h	M_w g.mol^{-1}	MMD
1/1,09	0	-	-
1/1,15	2300	260 000	2,7
1/1,3	6000	310 000	3,4
1/1,5	1600	340 000	3,5
1/1,8	1300	410 000	4,2
Commercial MAO (Al/Zr = 2000)	3000	380 000	3,6

Table 2 : Ethylene polymerization in the presence of racEt(Ind)$_2$ZrCl$_2$ activated by MAO** (MAO** prepared by reaction of benzophenone with TMA) Et(Ind)$_2$ZrCl$_2$ = 0.8 x 10^{-6} moles, Pethylene = 1bar , toluene = 100 mL, time = 1 h, temperature = 30°C,

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