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Priority Communication

Understanding the role of aluminum-based activators in single site iron catalysts for ethylene oligomerization

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ABSTRACT

In a combined experimental and theoretical study, the activation process of a single site ethylene oligomerization catalyst with aluminum-based activators has been studied. The results put forward a plausible deactivation reaction path of the catalyst for trimethylaluminum, while for methylaluminoxane and a novel phenoxyaluminum-based activator, the experimental catalyst's activity correlates with the energy barrier for the ethylene insertion.

1. Introduction

Methylaluminoxanes (MAO) [1–4] have been widely used as activators of ethylene oligomerization and polymerization iron-based catalysts, especially those belonging to the bis(imino)pyridine family, affording highly productive catalytic systems [5–12]. As high MAO/metal ratios are required, leading to high costs, considerable efforts have been undertaken to replace them in oligomerization reactions [13–15]. This requires a good understanding of the activation process of the catalyst. However, the identification of the precise role and active center of MAO during the activation process is hampered by the multitude of aluminum species present in solution [16,17], the control of the reaction exothermicity, along with the catalyst degradation and polymer byproduct formation.

In this communication, we report a well-defined dimeric aluminum complex $[PhOAlMe_2]_2$ and its activity for ethylene oligomerization using $(\{2,6\text{-}(2\text{-}(CH_3)C_6H_4N{=}C(CH_3))_2{-}C_5H_3N\}Fe(II)Cl_2)$ (abbreviated as $LFeCl_2$) precursor in comparison with the MAO and trimethylaluminium (TMA) cocatalysts. We furthermore present the DFT simulations that help to explain the observed experimental activities. $[PhOAlMe_2]_2$ and TMA are structurally well-defined aluminum species, whereas MAO is not. For the latter, a previously described model is therefore used (Scheme 1, structure (iii) in the lower rectangular box) [18–20].

While the iron-catalyzed oligomerization mechanism is largely accepted to follow a Cossee–Arlman type mechanism, leading to a Schulz–Flory distribution of linear α-olefins, the debate concerning the nature of the metallic active species and the corresponding activation path remains open and is fueled with numerous studies regarding the oxidation state of the active species or the non-innocence of the ligand toward redox reactions [21–26]. For example, $[LFe(II)Me]^+$ was observed by mass spectrometry along with other cationic species after activation of $[LFe(II)Cl_2]$ by MAO. We here assume a high-spin ferrous iron cationic species after activation with a redox-innocent neutral bis(imino)pyridine chelate and suppose no electron transfers between the metal and ligand.

2. Materials and methods

Methylaluminoxane (MAO 10 wt% in toluene) and TMA (trimethylaluminum) were purchased from Chemtura, while $[PhOAlMe_2]_2$ was obtained by addition of an equimolar amount

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of phenol to TMA in *n*-heptane in good yield (97%) and was characterized by ^{1}H and ^{13}C NMR and XRD [27]. [LFe(II)Cl_2] was prepared according to the procedure described in Ref. [28].

A toluene solution containing [LFe(II)Cl_2] (10 μmol) was injected in the autoclave under an inert nitrogen atmosphere, followed by the cocatalyst solution. The ethylene pressure was immediately increased to 30 bar, the temperature to 50 °C, and the mixture was mechanically stirred. Additional details are provided in the Supplementary materials.

DFT calculations were carried out with the unrestricted M06 functional [29], proven to provide an accurate description of aluminoxanes [30] as well as the spin state of the iron catalyst (Table 5S), in combination with Los Alamos pseudopotential and associated valence basis set on iron atoms [31] and the basis set 6-31G(d,p) for the other atoms. We have verified that the inclusion of solvent effects or expansion of the wave-functions over larger basis sets does not change the conclusions presented below from results of gas phase DFT calculations. This is in line with the theoretical findings of Zurek and Ziegler who also concluded that relative energies were not impacted by the inclusion of a solvent model [19]. Further details are presented in the Supplementary materials.

3. Results and discussion

Zero oligomerization activity was observed with the [LFe(II)Cl_2]/TMA system, even with an Al/Fe molar ratio of 500, while at the same ratio an activity up to 1.4×10^{5} g (mol(Fe) h)$^{-1}$ was measured with [$PhOAlMe_2$]$_2$. Ideally, lower Al to Fe ratios are sought after, as put forward in the introduction, but this leads to lower oligomerization activities.

A Schulz–Flory distribution ($K = 0.68$) of linear α-olefins was afforded comparable to the one observed when the activation is performed with MAO (Al/Fe = 250, $K = 0.69$). This latter catalytic system showed a higher, up to 7.4×10^{7} g (mol(Fe) h)$^{-1}$, activity. Nevertheless, the iron bis(imino)pyridine/MAO system is temperature-sensitive and coupled to the important exothermicity of the reaction, processing issues are encountered even at low catalyst loading. In our case, more than 40 wt% of the formed products are waxes and polyethylene (PE) with this system, while none of these heavy products were obtained with [$PhOAlMe_2$]$_2$.

As [$PhOAlMe_2$]$_2$ is a structurally well-defined cocatalyst, it serves as a very good candidate in this theoretical study to help to elucidate the activation mechanism of the precatalyst using MAO.

[LFe(II)Me]$^{+}$ may be obtained from [LFe(II)Cl_2] after a transfer of the two chloride anions to the cocatalyst, which becomes either mono- or dichlorinated, while Fe(II) gets mono-methylated. These initial steps have been studied with DFT calculations for the TMA and [$PhOAlMe_2$]$_2$ cocatalysts. Only minor energy differences between the reaction intermediates were found for both systems, thus not explaining the experimental activity difference. Since moreover, the complete dissociation of the created cationic iron species and the anionic cocatalyst is prohibitively costly, we will focus on the reactions of the ion pair, that is, cationic monoalkyl [LFe(II)Me]$^{+}$ and investigate its interactions with the three cocatalysts, each being mono- or dichlorinated (Fig. 5S) as well as with ethylene.

Table 1
Calculated Gibbs energies (kcal mol^{-1}) to form the mono- and dichlorinated anionic cocatalyst.

	[$PhOAlMe_2$]$_2$	TMA dimer	[AlMeO]$_6$[$AlMe_3$]
Monochlorinated	13.2	−0.6	5.9
Dichlorinated	11.6	6.5	2.4

Table 1 shows that only the formation of the monochlorinated TMA anion is an exergonic reaction. For [$PhOAlMe_2$]$_2$ and the MAO model, chloride anion formation is endergonic, and moreover, the dichloride anion is thermodynamically slightly more stable. Since the energy difference is small between the mono- and dichlorinated anion both intermediates will be considered in this study. This endergonicity puts forward an additional reason[1] why such large excesses of [$PhOAlMe_2$]$_2$ and MAO are needed to activate.

In the following, we assume that each cocatalyst is able to generate the [LFe(II)Me]$^{+}$ species; we first show how the nature of the anion influences the ethylene insertion mechanism: (**II**) → (**III-a**) in Scheme 1. In parallel, we explore possible routes leading to the catalyst deactivation: (**II**) → (**III-b**), (**II**) → (**III-c**), and (**II**) → (**III-d**).

The ethylene uptake by (**I**) yields intermediate (**II**), where the coordinated ethylene can be inserted in the Fe—C^{1} bond to give (**III-a**). The intermediates and transition states (**II-a**‡) for the insertion of ethylene into the Fe—C bond were optimized in the presence of the different chlorinated anionic activators (Fig. 6S). For each ion pair, an equatorial and axial approach (Fig. 4S) of the ethylene molecule has been evaluated and only the most stable π-complex was retained. The calculated Gibbs energies for different optimized intermediates and transition states are reported in Fig. 1.

The ethylene uptake is endergonic for all ion pairs obtained from the activation with the three different mono- or dichlorinated anions, note that the reported energies are relative to the energies of the ion pair and ethylene molecule at infinite distance. Considering the monochlorinated counter ions, the Gibbs energy barriers for the ethylene insertion are 16.8, 24.9, and 29.4 kcal mol^{-1} for respectively [AlMeO]$_6$[$AlMe_3$], [$PhOAlMe_2$]$_{2,}$ and TMA. Interestingly, the energy barrier for the insertion with the MAO model is even slightly lower than the value obtained for the bare cationic π-complex ($\Delta G^{\ddagger} = +19.1$ kcal mol^{-1}). However, the relative energy is lower for the bare complex.

The energy barrier for ethylene insertion is influenced by different parameters, like the interaction of the π-complex with the counterion. Hence, the smaller dissociation energy of the anion, that is, 60.7, 67.8, and 81.0 kcal mol^{-1} for respectively, MAO, [$PhOAlMe_2$]$_{2,}$ and TMA, the lower the barrier. Also the change in the C—C ethylene distance going from the π-adduct to the transition state convincingly correlates with the energy barrier: the smallest changes are observed for the smallest barrier energies, where the ethylene is weakly coordinated, for example, in the bare complex and in the presence of the MAO (see Table 3S and Fig. 2S).

The effect of the presence of dichlorinated anions on the uptake of ethylene and the insertion path has also been calculated. Especially, the formation of the π-adduct in the presence of the dichlorinated phenoxy species, [$Al_2Ph_2O_2Me_3Cl_2$]$^{-}$, becomes disfavored: $\Delta G_r = +13.7$ kcal mol^{-1} (Fig. 1S) with respect to the monochlorinated form ($\Delta G_r = +13.7$ kcal mol^{-1}). With a barrier of 20.7 kcal mol^{-1} for the ethylene insertion, the TS consequently gets as well significantly destabilized, making the overall insertion step slightly endergonic ($\Delta G_r = +2.0$ kcal mol^{-1}). Since [$PhOAlMe_2$]$_2$ experimentally does activate [LFe(II)Cl_2], we conclude that the monochlorinated anion is involved in the activation process, as it exhibits the more favorable (kinetic and thermodynamic) pathway. The dichlorinated form of TMA and MAO influences considerably less the stability of the π-complex and the insertion barrier, as can be seen from Fig. 1S.

The free energy barrier for ethylene insertion is lower in case of [AlMeO]$_6$[$AlMe_3$] than for [$PhOAlMe_2$]$_2$ or TMA, thereby providing an explanation for the higher experimental oligomerization

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[1] Other evoked reasons are the partial "loss" of MAO due to reactions with impurities (scavenger effect, Ref. [4]) and minor presence of reactive aluminum sites in MAO oligomers, as shown in Ref. [30].