INVESTIGATING & IMPROVING MAO ACTIVATION EFFICIENCY OF METALLOCENES FOR OLEFIN POLYMERIZATION

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Abstract

Group 4 transition metal-based molecules, particularly the metallocene dichlorides [Cp₂MCl₂], are industrially important as singleprecursors for alpha-olefin site catalyst polymerization. To be useful catalysts for polymerization the dichlorides require activation via alkylation/ionization chemistry in order to form the catalytically active ion pair {[Cp₂M- $R]+[A]-\}.$ Typical activators include methylaluminoxanes (MAO), borates {e.g. $[B(C_6F_5)_3]$ and boranes {e.g. $[Ph_3C][B(C_6F_5)_4]$ } combination with organoaluminum in compounds such as trimethyl-, triethyl- and triisobutyl-aluminum. While the MAO activation mechanism is not fully understood recent studies have suggested several plausible pathways.¹⁻⁴ The use of boron-based activators can often provide useful discrete molecular models to aid in this understanding. However, the structures of the activator and the metallocene must still be taken into account. Recent experiments suggest potential differences in MAO- vs. B-based activation mechanisms. Through these types of fundamental studies it's now believed to be better understood how to improve the overall activation efficiency of single-site catalysts with MAO. Furthermore, in combination with high-throughput (~ 1 gram) and lab-scale (~100 gram) polymerization methods, these improvements can be tested, refined and advanced in scale such as, for example. Grace's proprietary ActivCat® portfolio.

Introduction

Recent reports have suggested the initial mechanistic step in the ubiquitous MAOactivation of Group 4 metallocene dichloride pre-catalysts is ionization via abstraction of an $[AlMe_2^+]$ moiety from the MAO co-catalyst (Figure 1).^{5,6} This contrasts with other hypotheses that alkylation by organoaluminum occurs first followed by Lewis acid sites in MAO abstracting the R- or Cl-group to activate/ionize the transition metal.¹ Both cases appear to lead to the same ionized (μ -Me)₂ NMR observable catalyst resting state product.

The structure of MAO is not completely understood. However, the use of boron-based activators can often serve as molecular models for MAO-based systems thus allowing for the isolation, characterization and study of discrete species often inferred to be present in analogous MAO-based systems.

Results and Discussion

Reaction of rac-(ebi)ZrCl₂ 1 with a mixture containing one equivalent each of trimethylaluminum (TMA) and $[Ph_3C][B(C_6F_5)_4]$ affords 2 (Figure 2) in nearly quantitative yield as a dark solid. The molecular structure of 2 was established by NMR and Xray analysis (Figure 3). To our knowledge this is the first structurally characterized example of a metallocene dichloride in the +4 oxidation state coordinating an [AlMe₂⁺] moiety.⁷ Although so far not observed experimentally, a hypothesis is 2 also could initially form in MAO-activated systems, which would support the proposed $[AlMe_2^+]$ abstraction mechanism.

However, reaction of **1** first with TMA followed by $[Ph_3C][B(C_6F_5)_4]$ affords a mixture of **2** and **3** with the relative amounts of each being determined by the amount of TMA used relative to **1** (Figure 2). In this case monoalkylation by TMA⁸ clearly is occurring first, followed by ionization. Interestingly, no cationic $[\mu-(Me)(Cl)]$ species is observed. In order to form **3** as the majority product a large excess of TMA is required to drive the alkylation equilibrium reaction and overcome a competing disproportionation reaction. This may be related

to the reason why a large excess of MAO is typically used to achieve best performance in metallocene-based catalyst systems. Species like **3** are the believed resting state in metallocene catalyzed olefin polymerization. While routinely observed spectroscopically in both MAO- and boron-activated systems⁹ only recently have Group 4 metal species such as **3** been structurally characterized (Figure 4).^{10,11} Further support that alkylation is occurring first in the borate activator case is the reaction of *rac*-(ebi)Zr(Me)Cl with borate followed by AlMe₂Cl (Figure 5) which cleanly gives **2**.

Reaction of **1** with TMA followed by 0.5 equivalents of borate (Figure 6) affords cationic bimetallic species **4** which has been structurally characterized (Figure 7). This reaction can be thought of as a simulation of MAO activation at low Al/Zr ratios. While NMR data for species such as **4** have been reported in the literature¹² to our knowledge the molecular structure of such a species has not been reported. Attempts to prepare cationic heterobimetallic molecules via similar reactions will be discussed but have thus far been unsuccessful.

Conclusions

Based on results from fundamental studies using boron activators as models the polyolefin polymerization performance of supported MAOactivated metallocene catalysts can be improved without significantly impacting important polymer physical properties. For example, (Figure 8), at similar MAO and metallocene loadings the performance of some supported mPE and mPP metallocene catalysts can be increased dramatically.

References

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Figures and Tables



Figure 1. Proposed MAO activation mechanisms.



Figure 2. Reaction of metallocene with TMA and tritylborate.



Figure 3. Molecular structure of **2**.



Figure 4. Molecular structure of **3**.



Figure 5. Reaction of mono-methyl with borate followed by AlMe₂Cl.



Figure 6. Reaction of rac-(ebi)ZrCl₂ with TMA followed by 0.5 equiv. borate.



Figure 7. Molecular structure of 4.



Figure 8. Kinetic profile comparison of a supported ActivCat® MAO-based metallocene catalyst system versus reference catalyst.