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Alkylation and activation of metallocene polymerization catalysts by reactions with trimethylaluminum: A computational study

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ABSTRACT

Reactions between trimethylaluminum and selected zirconocene and hafnocene polymerization catalysts have been computationally studied at the MP2/TZVP level of theory. Dichloride precatalyst alkylation and the subsequent activation by ligand abstraction with trimethylaluminum were explored as a function of the catalyst structure. The alkylation reactions were found to proceed via two alternative routes depending on the structure of the catalyst. Concerning the activation of the alkylated precatalyst, interaction between trimethylaluminum and metallocene weakens the metal–ligand σ-bond, hence facilitating olefin uptake to some extent. Modification of the chemical environment of the Lewis-acidic Al site towards environments likely present in methylaluminoxane further facilitates the reaction, supporting the critical role of methylaluminoxane in catalyst activation.

1. Introduction

Group 4 metallocenes are industrially important catalysts for polymerization of α-olefins. Formation of a catalytically active species requires a cocatalyst, typically an alkylaluminoxane or a boron compound. The most effective, and the most widely used, cocatalyst is methylaluminoxane (MAO) [1]. Unfortunately, the precise structure and composition of MAO is unknown, holding back the understanding of its exact function and the mechanism of catalyst activation. According to the prevailing knowledge, the activation mechanism involves formation of a weakly coordinated ion pair through abstraction of a ligand from a metallocene precursor by a Lewis-acidic site of the MAO [2,3].

MAO is typically produced by partial hydrolysis of trimethylaluminum (TMA) [1]. Consequently, the produced MAO contains TMA, either as associated to the core structure of MAO or as free molecules [4–6]. While the exact role of TMA in the catalytic process is not well understood, there is a wealth of evidence that the type and the amount of TMA have notable effects on the function of the cocatalyst. While TMA has been shown to monoalkylate dichloride catalyst precursor, [7–13] its role in the activation process itself is elusive. Usually TMA is found to reduce the activity of the catalysts, [7–11] but addition of TMA has also been reported to increase the activity, [14,15] or even to act as the actual cocatalyst [4,15]. A number of related computational studies have been reported on aspects concerning ligand abstraction, ion pair formation and monomer incorporation with various cocatalysts and catalyst precursors [10,13,16–25]. The detrimental role of TMA is widely discussed in the literature and both experimental and computational studies suggest that TMA is responsible for low molecular weights and formation of dormant catalytic sites, inhibiting the chain growth [3,14,26–29]. Apparently, the presence of TMA affects all key steps of the process.

The role of TMA in the process is likely dependent on the structure of the catalyst, being affected by both the central metal and the ligand structure of the metallocene. Zirconocenes and hafnocenes are both isoelectronic d^0 complexes, with similar ionic radii and electronegativity [30]. Despite the structural similarity, their catalytic behavior in MAO-activated processes is often very different; zirconocene are generally more active but hafnocenes typically produce higher molecular weight polymers [31–36]. This has been attributed to the strength of the σ-bond between the central metal and carbon, which is weaker for Zr, [37] also affecting the reactivity towards aluminum compounds. Likewise, the ligand structure of the metallocene, due to both steric and electronic contributions, affect the strengths of the metal–ligand bonds and hence their reactivity [38–40].

To shed light on the questions concerning the fundamental reactions between TMA and metallocene precursor in the catalytic

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process, a quantum chemical study is reported. The study focuses on elementary reactions between trimethylaluminum and metallocene precatalyst in terms of creating a catalytically active species: precatalyst alkylation (ligand exchange between TMA and metallocene) and activation of the alkylated precatalyst (ligand abstraction by TMA). Furthermore, the consequence of modification of the chemical environment of the aluminum towards sites likely present in MAO is explored. Four metallocene precatalysts are included in the study to also address the influences of the central metal and the ligand framework on the reactions.

2. Computational methods

Correlated ab initio methods are necessary for proper treatment of TMA, which is due to the bridging pentavalent methyl groups [41]. The RI-MP2/def-TZVP [42–44] method was employed throughout the work because it has turned out a cost-effective choice concerning the structure of TMA [45]. All calculations were performed by TURBOMOLE V6.2 [46]. The stationary points in the potential energy surface were characterized as either minima or transition states by frequency calculations, also required for calculation of Gibbs free energies ($T = 298.15$ K, $p = 101.325$ kPa).

3. Results and discussion

Four catalyst precursors (Fig. 1) were included to study the effects of the central metal and the ligand framework: Cp_2ZrCl_2, Cp_2HfCl_2, $Me_2CCpFluZrCl_2$, $Me_2CCpFluHfCl_2$. The latter ligand framework represents a typical catalyst used in industry.

3.1. Trimethylaluminum

Depending on the conditions, TMA can exist either as a monomer or as a dimer (Fig. 2). In room temperature, the equilibrium lies on the side of the dimer (calculated ΔG^{θ} for the dimer to monomers dissociation is 14 kJ/mol). Increase in the temperature shifts the equilibrium towards the monomer. Due to the preparation process, the solutions of MAO contain residual free TMA, which in typical polymerization temperatures exists mainly as a dimer [47]. According to NMR measurements, most of the TMA is associated to MAO, [48] thereby being in monomeric form, and in equilibrium with the free TMA according to equation (1). Regarding associated TMA, the saturative four-coordination of the aluminum has been proposed to be attainable through bridging methyl groups similar to the structure of the TMA dimer. These so-called latent Lewis-acidic sites [49] could generate reactive and catalytically active three-coordinated Al centers through opening of the methyl bridge [10,11,45]. It follows that in the investigations of the reactions of TMA both the monomer and the dimer structures have to be addressed.

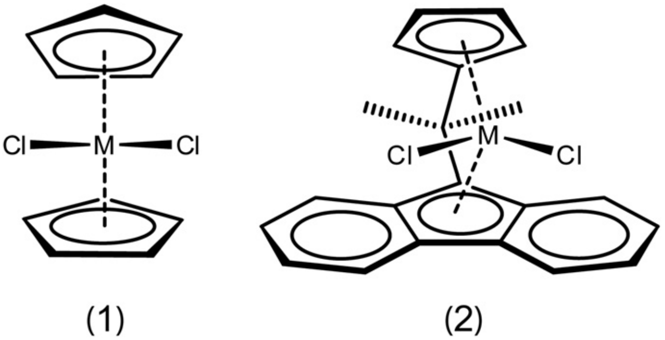

Fig. 1. Metallocene dichloride precatalysts included in the study (M = Zr, Hf): (1) Cp_2MCl_2 and (2) $Me_2CCpFluMCl_2$.

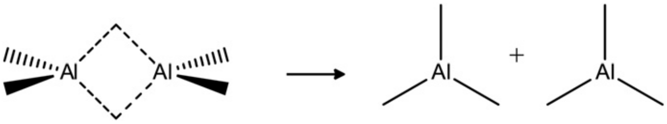

Fig. 2. Dissociation of Al_2Me_6.

$$MAO \cdot n(AlMe_3) \rightarrow MAO \cdot (n-m)(AlMe_3) + (m/2)Al_2Me_6 \qquad (1)$$

3.2. Metallocene dichloride alkylation

Upon introduction of metallocene dichloride precursor and TMA, alkylation by ligand exchange is observed in experiments, yielding a monomethylated metallocene and an alkylaluminum chloride (Fig. 3) [7–13]. In the ligand exchange reaction, the electron deficient aluminum partially abstracts the chloride ligand from the metallocene, reducing the electron density of the central metal, thereby making the metal to abstract the methyl group from TMA, in turn. The monoalkylated metallocene precursor can then be activated by a Lewis acidic cocatalyst (see Chapter 3.3). Alternatively, the formed metallocene monoalkyl can undergo another ligand exchange reaction, resulting in a dimethylated metallocene. Here we focus on the monoalkylated precatalyst.

3.2.1. Comparison of the reaction pathways

Trimethylaluminum (either $AlMe_3$ or Al_2Me_6) coordinates to metallocene dichlorides in two orientations: either from the front or from the side, as illustrated in Fig. 4 (for $AlMe_3$) and Fig. 5 (for Al_2Me_6). Both complexes were considered as starting points for the ligand exchange reaction. The potential energy surfaces of the reactions were mapped by simultaneous modification of aluminum–chlorine and metal–methyl distances. From the two relative orientations of $AlMe_3$ and metallocene dichloride (A and D in Fig. 4) the reaction can proceed through two different transition

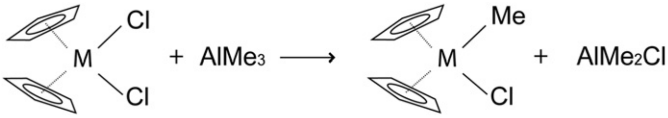

Fig. 3. Schematic presentation of the metallocene dichloride monoalkylation process.

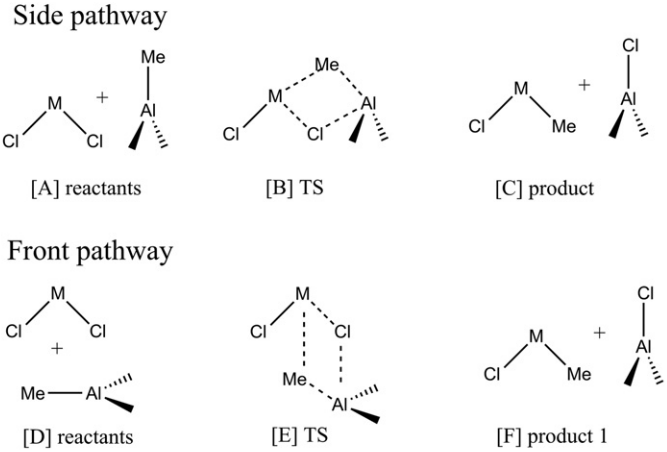

Fig. 4. Schematic presentation of the alkylation of the metallocene with $AlMe_3$. Metallocene ligand framework is omitted for clarity.