Activation Reactions of Cp₂ZrCl₂ and Cp₂ZrMe₂ with Aluminium Alkyl Type Cocatalysts Studied by in situ FTIR Spectroscopy

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Abstract. The reactions of Cp₂ZrCl₂ and Cp₂ZrMe₂ with methylaluminoxane (MAO), trimethylaluminium (TMA) and dimethylaluminium chloride (DMAC) have been investigated by in situ FTIR spectroscopy. The studies have been performed in a cell that allows continuous monitoring of the reactions and stepwise additions of reactants. Most bands of the zirconocenes are unaffected by the reactions, but a strong Cp band at 803-822 cm⁻¹ was found to give distinct information on structural changes in the zirconocenes. A slow formation of the monochloro-monomethyl compound Cp₂ZrClMe from a mixture of Cp₂ZrCl₂ and Cp₂ZrMe₂ has been verified. Only weak complexes are formed in mixtures of zirconocenes and TMA or DMAC. The chemical potential for methylation of zirconocenes is primarily due to MAO clusters, but TMA may be important in the mechanism. Our IR data is consistent with the formation of stable compounds during activation, which we assume include methyl or chlorine bridges between zirconium and aluminium, but do not differentiate between ionic or neutral complexes. Observed disappearance of C–H stretching bands may indicate double bridges between zirconium and aluminium.

Introduction

The present study is part of a more extensive FTIR spectroscopy work where all binary mixtures in the system Cp₂ZrCl₂, Cp₂ZrMe₂, TMA, DMAC and MAO have been investigated. Earlier we have shown that MAO and TMA behave as independent stable structural entities in mixtures, that may exchange ligands, but which do not form new compounds.[1] This study revealed the presence of bridging methyl groups on the surface of stable MAO clusters, for which we recently have proposed molecular structures.[2] It was also found that MAO when reacted with DMAC loose the bridging methyl groups, and change to a chlorinated MAO that is not able to activate olefin polymerisation with (C₅Me₅)₂ZrCl₂.[3]
In the present work the reactions between the aluminium compounds and the metallocenes are studied, and the studies have been conducted to reveal – if possible – changes both in the metallocene and the aluminium compounds. Fig. 1 depicts all binary mixtures in the system. The figure also indicates which mixtures lead to formation of new compounds (lines), and which do not (dashes).

![Diagram](image)

**Fig. 1.** Binary combinations in the system Cp₂ZrCl₂, Cp₂ZrMe₂, TMA, DMAC and MAO. Dashed lines indicate binary systems where no new compounds were observed.

The formation and the nature of the active centre for polymerisation have been much discussed in the research literature [4-11], and partly covered in a recent review.[12] In general, the formation of cationic active centres is suggested to involve a fast mono-methylation of the metallocene, if a chloride is used, followed by a slow ion pair formation by abstraction of a chloride ion.[12] Theoretical studies have shown that the ion pair formation and separation is not energetically favourable without a large anionic counterion to spread the negative charge as well as solvent or monomer coordination to the cation.[7] Several options for complexation to the cation is offered by MAO – through oxo,[4,5,22,23] methyl [11] or chlorine[6,7] bridges, or by formation of a methylene bridge.[5] In addition, the methyl-bridged binuclear cations, 

\[(\text{Cp}_2\text{ZrMe})_{\mu-\mu}\text{Me}]^+ \text{ and } [\text{Cp}_2\text{Zr}(\mu-Me)\text{Me}_2\text{AlMe}_3]^+ , \]

have been proposed.[8,10] Mostly, these complexes have been suggested to be dormant sites, but MAO has also been suggested to be an important part of architecture of the active site.[4,5,22] Bonds between MAO and the neutral zirconocene have also been suggested. A recent NMR study indicates a fast equilibrium where Cp₂ZrMe₂ and MAO form a methyl-bridged non-ionic complex at low Al/Zr ratios.[11] Calculations on the formation of a chlorine-bridged compound Cp₂ZrMe(μ-Cl)AlMe₃ and "Cp₂ZrMe(μ-Cl)MAO" (model structure) have been reported.[7] The former complexes were calculated to be unstable and the latter stable.

Unfortunately, detailed information on the structural changes of MAO during activation and the interaction with zirconocenes is not easily obtained. The otherwise powerful NMR spectroscopy has not been particularly useful, partly due to extremely broad NMR peaks of MAO.[6,10,22] The low concentration and the fluxional nature of the interactions introduce further difficulties.

The study of such interactions is important in order to understand the activation process in the zirconocene/MAO system. While a large number of metallocenes have been studied by IR spectroscopy,[13] hardly any such data exist for catalyst systems used in olefin polymerisation[14].