Physicochemical surface-structure studies of highly active zirconocene polymerisation catalysts on solid polymethylaluminoxane activating supports†

Alexander F. R. Kilpatrick, Nicholas H. Rees, Zoë R. Turner, Jean-Charles Buffet and Dermot O’Hare*

Physicochemical surface-structure studies of highly active slurry-phase ethylene polymerisation catalysts has been performed. Zirconocene complexes immobilised on solid polymethylaluminoxane (sMAO) (sMAO–Cp₂ZrX₂), have been investigated using SEM-EDX, diffuse reflectance FT-IR (DRIFT) and high field (21.1 T) solid state NMR (ssNMR) spectroscopy. The data suggest a common surface-bound cationic methylzirconocene is the catalytically active species. ⁹¹Zr solid state NMR spectra of sMAO–Cp₂ZrCl₂ and sMAO–Cp₂ZrMe₂ are consistent with a common surface-bound Zr environment. However, variation of the σ-donor (X) groups on the metalocene precatalyst leads to significant differences in polymerisation activity. We report evidence for X group transfer from the precatalyst complex onto the surface of the aluminoxane support, which in the case of X = C₆F₅, results in a 38% increase in activity.

Introduction

Methylaluminoxane (MAO) is the most commonly used activator and co-catalyst for transition metal containing, single-site complexes in olefin polymerisation.¹,² The combination of MAO, an inert inorganic carrier material (most commonly silica) and a precatalyst complex have been described by Severn as the “Holy Trinity” of supported single-site catalysts.³ However, there is also growing interest in single-site catalysts in particle forming polymerisation processes that are free from an inert inorganic carrier.⁴ These require an activating support material, which can be combined with the precatalyst complex in a single synthetic step.⁵⁻⁷ This process has several advantages from an industrial viewpoint, as it reduces the time and energy-intensive drying steps and hence can lower manufacturing costs. Furthermore, these ‘self-supported’ catalyst systems have an advantage over silica-supported systems as the complex loading can be increased significantly, which leads to correspondingly higher polymerisation activities.

In 2013, Tosoh Finechem Corporation reported, in the patent literature, an insoluble form of solid methylaluminoxane (sMAO) formed via controlled hydrolysis of trimethylaluminium with benzoic acid.¹⁰ We have recently reported the laboratory scale synthesis and detailed characterisation of sMAO,¹¹ and demonstrated its function as a solid-phase support, scavenger and activator in slurry-phase ethylene polymerisation.¹²⁻¹⁴ Observed activities are significantly higher than for other supports; for example sMAO-rac-ethylenebis[1-permethylindenyl]zirconium dichloride is at least three times more active than its silica-supported MAO counterpart (5365 vs. 1649 kgₘₚₙₐₜ⁻¹ h⁻¹ bar⁻¹ respectively).¹⁵,¹⁶

Furthermore, we have shown that reaction of sMAO with tris(pentafluorophenyl)borane or pentafluorophenol produces highly active modified-sMAO supports which show enhanced polymerisation activity with both rac-ethylenebis(1-indenyl) zirconium dichloride, rac-(EBI)ZrCl₂,¹⁷ and a range of unsymmetrical anza-bridged permethylindenyl complexes.¹⁸

Characterisation of sMAO using multinuclear NMR spectroscopy in solution and in the solid state reveals an aluminoxane structure that features “structural” and “free” AlMe₃ units in addition to benzoate residues. Total X-ray scattering measurements on sMAO allow comparisons to be made with simulated data from DFT modelled structures of MAO. Of these, the best fit to the experimental X-ray scattering data resulted from TMA-capped nanotubular and spherical cage structures, (AlOMe)ₙ⁹ (AlMe₃)₃ and (AlOMe)₂₀(AlMe₃)ₙ, n = 1, 2, respectively.¹⁹,²⁰

Our current efforts are focussed on elucidating the structure and chemical environment of the active polymersing species in sMAO supported catalysts. Significant progress has been made in the last few years to determine the function of MAO as a
source of the electrophilic cation [AlMe₂]⁺, which plays a key role in the activation of metallocene complexes in solution.21–31 Weckhuysen and co-workers have recently proposed a similar mechanism which operates in the genesis of the active site for [1,3-nBu,Mo]Cp₂ZrCl₂ immobilised on silica–MAO (Scheme 1).32,33 Specifically, metallocene activation occurs by the complexation of the precursor with weak Lewis acid sites of silica–MAO, which are a source of mobile [AlMe₂]⁺ groups, leading to formation of the active cationic zirconocene species stabilised on the surface by MAO.

This has prompted us to investigate in more detail the nature of the active species generated in sMAO supported zirconocene systems. We have chosen a series of zirconocene(ν) precatalyst complexes due to the relative simplicity of their ligand environment, which allows more facile characterisation, and enables comparison with previous studies of the active species in homogeneous and heterogeneous single-site catalyst systems.34–37

We have employed a combination of characterisation methods, including high field solid state nuclear magnetic resonance (ssNMR) spectroscopy, SEM-EDX elemental mapping and diffuse-reflectance FT-IR spectroscopy. Through these fundamental investigations into the active species, we aim to establish structure/catalytic activity relationships for the immobilised complex and solid support.

Results and discussion

Catalyst synthesis and characterisation

A series of zirconocene(ν) complexes, Cp₂ZrX₂ (X = Cl, Me, Br, Ph, C₆F₅, O₅C₆F₅), nBuCp₂ZrCl₂, rac-(EBI)ZrCl₂, Me₂Si(C₅H₄)₂ZrCl₂, and Me₂Si(C₅H₄)₂ZrMe₂ were selected as precatalysts for this study. In each case, the supported complex–sMAO sample was synthesised by addition of toluene to a mixture of solid support and complex (initial loading [AlsMAO]₀/[Zr]₀ of 50), followed by heating at 80 °C for 1 h. After workup, bright orange powders were isolated in >85% yield (Scheme 2).

Elemental analysis of these catalysts using ICP-MS is presented in Table 1. The aluminium content of the final catalysts remains approximately constant across the series, slightly reduced from that of the sMAO support (40.2 wt%). For all sMAO–Cp₂ZrCl₂ catalysts, the [Al sMAO]₀/[Zr]₀ molar ratio determined was close to the targeted ratio of 50, consistent with full complex immobilisation. This confirms that the degree of immobilisation of zirconocene dichloride complexes is not affected by the different ancillary Cp₈ ligands. This can be attributed to the high surface area (ca. 600 m² g⁻¹) and reactivity of sMAO in which all surface sites can activate zirconocene complexes. The high concentration of active “Al–Me” moieties is beneficial when compared to MAO-impregnated silica supports, which generally show a lower surface area (ca. 275 m² g⁻¹) and hence [Al sMAO]₀/[Zr]₀, loadings below 131 cannot be achieved without complex leaching and significant reactor fouling. Furthermore, inert carrier supports possess –OH groups which provide a pathway for complex deactivation.32,38 Comparison of the [Al sMAO]₀/[Zr]₀ data for chloride and methide complexes with the same Cp₈ ligands, Cp₂ZrX₂ and Me₂Si(C₅H₄)₂ZrX₂ (X = Cl, Me), reveals that both chloride and methide leaving groups result in near-quantitative complex immobilisation. However, the sMAO–Cp₂ZrX₂ catalysts derived from metallocones with aryl and aryloxide σ-donor groups (X = Ph, nBu₅F₅, O₅C₆F₅) show slightly higher [Al sMAO]₀/[Zr]₀ values, suggesting the larger leaving group limits the extent of complex immobilisation under these conditions.

Solid MAO is insoluble in aromatic and aliphatic hydrocarbons but is sufficiently soluble in THF-d₈ to be studied by solution NMR spectroscopy. However, efforts to apply solution NMR spectroscopy to characterise sMAO–complex samples was complicated by leaching of the zirconocene upon addition of THF-d₈.

Solid-state NMR spectroscopy has been increasingly applied for characterisation of supported organometallic complexes,39–41 and has proved a powerful tool for the structural elucidation of immobilised single-site zirconocene catalysts.34,35,42,43 For these experiments samples of sMAO–Cp₂ZrCl₂ (X = Cl, Me) with [Al sMAO]₀/[Zr]₀ = 25 were prepared according to Scheme 2, which produced brightly coloured solids that settled beneath a colourless supernatant solution. Elemental analysis by ICP-MS provided a zirconium content of 3.22 and 4.16 wt% for sMAO–Cp₂ZrCl₂ and sMAO–Cp₂ZrMe₂ respectively.

| Complex          | Al (wt%) | Zr (wt%) | [Al sMAO]₀/[Zr]₀ |
|------------------|----------|----------|-----------------|
| Cp₂ZrCl₂         | 36.2     | 2.36     | 51.7            |
| Cp₂ZrMe₂         | 37.0     | 2.32     | 53.9            |
| Cp₂ZrBr₂         | 34.1     | 1.71     | 67.4            |
| Cp₂Zr(C₆F₅)₂    | 34.2     | 1.78     | 65.1            |
| Cp₂Zr(C₆F₅)₂    | 35.1     | 1.73     | 68.6            |
| nBuCp₂ZrCl₂     | 34.4     | 1.69     | 68.8            |
| rac-(EBI)ZrCl₂  | 34.9     | 2.26     | 52.1            |
| Me₂Si(C₅H₄)₂ZrCl₂ | 35.7   | 2.08     | 58.1            |
| Me₂Si(C₅H₄)₂ZrMe₂ | 37.6   | 2.40     | 53.1            |

Table 1 Elemental analysis and ethylene polymerisation data for supported complex–sMAO catalysts at target loading [Al sMAO]₀/[Zr]₀ = 50.

Imobilisation conditions: sMAO–complex ([Al sMAO]₀/[Zr]₀ = 50), 80 °C, 60 minutes, toluene (30 mL). All elemental analysis experiments were conducted three times to ensure the reproducibility of the corresponding outcome.

The immobilisation conditions (sMAO–complex ([Al sMAO]₀/[Zr]₀ = 50), 80 °C, 60 minutes, toluene (30 mL)) were complicated by leaching of the zirconocene upon addition of THF-d₈. This has prompted us to investigate in more detail the nature of the active species generated in sMAO supported zirconocene systems. We have chosen a series of zirconocene(ν) precatalyst complexes due to the relative simplicity of their ligand environment, which allows more facile characterisation, and enables comparison with previous studies of the active species in homogeneous and heterogeneous single-site catalyst systems.34–37

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Samples of sMAO–Cp₂ZrCl₂ and sMAO–Cp₂ZrMe₂ show identical ¹H DEPTH ssNMR spectra (Fig. S6 and S8, ESI†) with resonances at δH ~ -0.4 and 6.8 ppm assigned to Al-CH₃ and Zr-CpH environments of the sMAO support and immobilised zirconocene species, respectively. ¹³C CP-MAS spectra of sMAO–Cp₂ZrCl₂ and sMAO–Cp₂ZrMe₂ (Fig. S5 and S7, ESI†) both show signals at ~7 and 177 ppm, assigned to the Al–methyl and benzoate groups in sMAO, and resonances at 114 and 128 ppm assigned to Zr-Cp environments. A broad resonance is observed at 50 ppm, in the expected region for a Zr–CH₃ group, however, the low intensity means we cannot be unequivocal in this assignment. An analogous sample synthesised with Cp₂Zr(¹³CH₃)₂ (Fig. 1) shows significant signal enhancement in the ¹³C CP-MAS spectrum at ~7 ppm and a relatively low signal enhancement at 50 ppm, suggesting the labelled methyl groups are scrambled with the Al–Me groups of the sMAO support.

Solid state ⁹¹Zr NMR is a logical choice for the characterisation of immobilised metalloocene catalysts. However, ⁹¹Zr ssNMR studies of organometallic zirconium complexes are rare owing to the relatively low sensitivity of ⁹¹Zr (I = 5/2), due to a low natural abundance (11.23%) and a relatively low gyromagnetic ratio (~2.49750 × 10⁷ rad T⁻¹ s⁻¹). Despite these challenges, Schurko and co-workers have reported in-depth ⁹¹Zr ssNMR studies of a range of zirconocenes, including olefin polymerisation precatalysts Cp₂ZrCl₂ and Cp₂ZrMe₂. However, no follow-up studies for ⁹¹Zr ssNMR characterisation of heterogeneous catalyst systems have been published, presumably owing to the low wt% Zr in supported complexes that are also active for polymerisation.

The Quadrupolar Carr Purcell Meiboom Gill (QCPMG) technique is a common method used to measure broad NMR signals from quadrupolar nuclei. The static QCPMG sub-spectra of sMAO–Cp₂ZrX₂ (X = Cl, Me) samples in a 7 mm o.d. silicon nitride rotor were acquired in a piecewise fashion using 51 420 Hz irradiation frequency offsets (integer multiple of 1/τₛ) until no further signal could be detected upon further increase or decrease of the transmitter frequency. The QCPMG experiment gives spectra in the form of a manifold of spikelets which are offset from the irradiation frequency by 1/τₛ; therefore, differentiation of nonequivalent sites by chemical shift is not possible unless gross differences (i.e., fairly distinct overlapping powder patterns) can be observed. The co-added spectra for pure Cp₂ZrCl₂ and Cp₂ZrMe₂ (Fig. 2a and b, respectively) show significant differences to each other, the latter complex showing a broader spikelet pattern consistent with a larger quadrupolar coupling constant (C₀). Spectra for immobilised complexes sMAO–Cp₂ZrCl₂ and sMAO–Cp₂ZrMe₂ (Fig. 2c and d, respectively) show complex spikelet patterns that are qualitatively similar, with breadths of 196 and 194 kHz respectively. Unfortunately, the chemical shift dispersion at B₀ of 21.1 T is insufficient to resolve if any non-equivalent Zr sites are present. Nonetheless, the clear similarities in the ⁹¹Zr ssNMR spectra of sMAO–Cp₂ZrCl₂ and sMAO–Cp₂ZrMe₂ are consistent with common surface-bound Zr environments, and provide a useful “fingerprint” for the supported complexes.

Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy was employed to further characterise the supported catalysts. The DRIFT spectra of sMAO–Cp₂ZrCl₂ and sMAO–Cp₂ZrMe₂ ([Al₃MAO]₀/[Zr]₀ = 25) both show strong IR bands at ca. 840 cm⁻¹ in addition to those of the sMAO support (Fig. S23, ESI†). An in-depth IR study of MAO–metalallocene reaction mixtures by Eilertsen et al. attributed IR bands around 820 cm⁻¹ to a cationic species containing a methyl bridge between Zr and Al, that is active for ethylene polymerisation. This provides supporting evidence for methylation of the Zr-Cl bond on immobilisation of Cp₂ZrCl₂ with sMAO.

The spatial distribution of Al, O, Zr and Cl on the surface of the immobilised catalysts was investigated by Scanning Electron Microscopy (SEM) together with Energy Dispersive X-ray (EDX) spectroscopy. An [Al₃MAO]₀/[Zr]₀ = 25 was required in order to observe the immobilised zirconium species (< 5 wt% Zr) by EDX spectroscopy. Elemental mapping of sMAO–Cp₂ZrCl₂ (Fig. 3) reveals a homogeneous distribution of Zr and Cl on the sMAO particles, and sMAO–Cp₂ZrMe₂ shows a similar distribution of Zr with no Cl detected. These data are consistent with a “single-site” Zr species that forms with concomitant transfer of a donor group, X⁻, onto an Al site on the sMAO support. In the case of sMAO–Cp₂ZrCl₂, homogeneous chlorination of the support could occur via direct Cl⁻ abstraction from the metalallocene dichloride precursor by strong Lewis acid sites in the solid activator. Alternatively, based on a [AlMe₂⁺]-assisted activation mechanism, sMAO chlorination could occur via net exchange of surface AlMe₂ sites for Al₂Me₃Cl, which is formed as a byproduct of catalyst methylation (Scheme 1).

**Slurry-phase ethylene polymerisation studies**

The series of sMAO-complex ([Al₃MAO]₀/[Zr]₀ = 50) catalysts were tested for slurry-phase ethylene polymerisation capability.

Comparing the activity data (Table 2) for supported zirconocene dichloride catalysts with different Cp₅ ligands reveals a wide range in activity values, with rac-[EBI]ZrCl₂ and Me₅Si(C₅H₄)₂ZrCl₂ displaying the highest and lowest activities,
respectively (3640 and 292 kgPE mol^{-1} h^{-1}). Comparing the activity data for sMAO–Cp₂ZrX₂ catalysts (X = Cl, Me, Br, Ph, C₆F₅, OC₆F₅) reveals a maximum for Cp₂Zr(C₆F₅)₂ and minimum for Cp₂ZrBr₂ (1160 and 516 kgPE mol^{-1} h^{-1} respectively).

In general, the sMAO–(EBI)ZrCl₂ catalyst produces polyethylene with lower molecular weights (Mₖ of 88.6 kDa) and slightly broader molecular weight distribution (MWD, Mₖ/Mₙ of 4.0) than the zirconocene catalyst systems with Cp R ligands (210 kDa < Mₖ < 277 kDa; 3.1 < Mₖ/Mₙ < 3.4). Despite the high [Al₄MAO]₀/[Zr]₀ loadings used in these heterogeneous systems, the absence of reactor fouling and good polymer properties can be attributed to single-site catalytic behaviour.

Differential scanning calorimetry (DSC) analysis of the polyethylenes produced by supported complex–sMAO catalysts based on Cp₂ZrBr₂, Cp₂Zr(C₆F₅)₂, Cp₂Zr(OC₆F₅)₂ and Me₂Si(C₅H₄)₂ZrCl₂ revealed crystallisation temperatures (T_c) between 116 and 117 °C during the first cooling cycle and melting temperatures (T_m) of 129–135 °C during the second heating cycle (Fig. 4 and Table S4, ESI†), indicative of HDPE with minimal defects and branching.¹²,¹³

| Complex               | Activity/10² (kgPE mol⁻¹ h⁻¹) | Productivity (kgPE g⁻¹ cat⁻¹ h⁻¹) | Mₖ (kDa) | Mₖ/Mₙ |
|-----------------------|-------------------------------|-----------------------------------|----------|-------|
| Cp₂ZrCl₂              | 9.54                          | 0.26                              | 205.9    | 3.4   |
| Cp₂ZrMe₂              | 10.5                          | 0.29                              | 202.6    | 3.3   |
| Cp₂ZrBr₂              | 5.16                          | 0.14                              | 276.9    | 3.0   |
| Cp₂Zr(C₆H₅)₂          | 9.78                          | 0.26                              | 232.2    | 3.2   |
| Cp₂Zr(C₆F₅)₂          | 11.6                          | 0.30                              | 229.3    | 3.2   |
| Cp₂Zr(OC₆F₅)₂         | 9.10                          | 0.23                              | 217.9    | 3.0   |
| n-BuCp₂ZrCl₂          | 19.3                          | 0.51                              | 218.0    | 3.1   |
| rac-(EBI)ZrCl₂        | 36.4                          | 0.69                              | 88.6     | 4.0   |
| Me₂Si(C₅H₄)₂ZrCl₂     | 2.92                          | 0.079                             | 44.8     | 3.5   |
| Me₂Si(C₅H₄)₂ZrMe₂     | 5.34                          | 0.15                              | 42.2     | 3.2   |

Table 2 Ethylene polymerisation and molecular weights data for supported complex–sMAO catalysts at target loading [Al₄MAO]₀/[Zr]₀ = 50

Polymerisation conditions: 10 mg catalyst, 2 bar C₂H₄, 70 °C, 30 minutes, [Al₄MAO]₀/[Zr]₀ = 1000, hexanes (50 mL). All polymerisation experiments were conducted at least twice to ensure the reproducibility of the corresponding outcome and mean activity values are quoted correct to 3 significant figures.

SEM imaging of the polyethylene samples reveals good morphology of the polymer despite the high [Al₄MAO]₀/[Zr]₀ loadings used in the catalysts. For the sMAO–Cp₂ZrCl₂ system ([Al₄MAO]₀/[Zr]₀ = 50), smooth popcorn-like polyethylene particles with low levels of aggregation are observed, which mimic the morphology of the catalyst particles (Fig. 5).

These slurry-phase polymerisation data are consistent with longstanding observations for solution phase MAO–zirconocene catalysts, namely that the ancillary Cp R has a primary effect on activity and polymer properties. However, our data show that the change of σ-donor group on the metalloocene also has a significant effect on catalyst performance.

In the sMAO supported catalyst system the postulated active species is a charged zirconocene species which is grafted onto...
the aluminoxide surface primarily by electrostatic interactions (Scheme 2). The steric and electronic demands of the CpR ligands bound to the zirconocene species are assumed to have a large influence on its relative stability, and hence on the rates of propagation and termination steps in the polymerisation reaction.

We have previously reported that modified sMAO supports, in which surface methyl groups are exchanged for C6F5 or OCF5 groups, result in activity increases with C6F5 and C6F5O groups on the support lead to an increase in separation between the charged species formed after zirconocene activation, which in turn enhances the performance of the catalytically active species. According to the proposed activation of a Cp2ZrX2 precatalyst by sMAO (Scheme 2) the σ-donor groups are transferred from zirconium onto the aluminoxide surface. In effect this produces a modified support which can have a secondary influence on the zirconocene species involved in the polymerisation.

To test this hypothesis, catalyst samples were synthesised from a pentafluorophenyl modified polymethylaluminoxane support, sMMAO(C6F5), and the dimethylzirconocene complex, Cp2ZrMe2 (Scheme 3). The corresponding modifier loading with respect to [AlsMAO]0 was selected to give an approximately equal concentration of C6F5 groups as the sMAO–Cp2Zr(C6F5)2 catalyst with target [AlsMAO]0/[Zr]0 loading of 25. Catalyst samples sMMAO(C6F5)–Cp2ZrMe2 (Cat A) and sMAO–Cp2Zr(C6F5)2 (Cat B) were characterised by SEM-EDX analysis and solid-state NMR spectroscopy and tested for ethylene polymerisation.

The 19F{1H} DEPTH SSNMR spectra of Cat A and Cat B (Fig. S13 and S22, ESI†) show very similar features, with resonances centred at −121, −162 (shoulder) and −166 ppm, assigned to aluminium bound C6F5 groups. Furthermore, the 19F{1H} NMR spectra of both Cat A and Cat B in THF-d8 solution (Fig. S2 and S4, ESI†) consist of three 19F resonances with identical chemical shift values (−123.2, −158.3 and −164.2 ppm). These 19F NMR spectra are also near identical to those of the C6F5 group transfer from Zr to Al in the immobilisation reaction.

The slurry-phase ethylene polymerisation activity data for Cat A and Cat B (Table S4, ESI†) are the same within error (772 and 776 kgPE molZr−1 h−1 respectively) and 38% higher than that of an unfluorinated control catalyst system sMAO–Cp2ZrMe2 (560 kgPE molZr−1 h−1). GPC analysis of the polyethylenes produced by Cat A and Cat B reveals similar molecular weights (Mw of 223.8 and 239.5 kDa respectively) and molecular weight distribution (Mw/Mn of 3.1 and 3.2 respectively), consistent with a common active species.

The observed activity enhancement is particular to the C6F5 complex-support system. Further polymerisation studies with sMAO–Cp2ZrCl2 and sMAO–Cp2ZrMe2 catalysts in a range of [AlsMAO]0/[Zr]0 ratios (300, 200, 100, 50 and 25) show similar activity values at each complex loading (Table S3 and Fig. S26, ESI†). In these cases, the difference between Cl or Me ligand transfer from complex to support does not significantly affect the polymerisation activity.

Conclusions

Solid methylaluminoxane, sMAO, has been shown to be an effective activating support for simple zirconocene complexes, Cp8ZrX4, up to a maximum [Al]0/[Zr]0 loading of 25. We attribute this to the high surface area (ca. 600 m2 g−1) and concentration of highly reactive and accessible “Al–Me” sites.
Such a high complex loading enables in-depth characterisation of the final functional catalyst that currently is not possible for zirconocenes with other MAO-impregnated inorganic supports. $^{13}$C CP-MAS ssNMR and DRIFT spectroscopy evidence herein points to a [Cp$_2$ZrMe]$^+$ species for the sMAO–Cp$_2$ZrMe$_2$ system. Moreover, static $^{91}$Zr ssNMR and DRIFT spectroscopy indicate that the same zirconium species is present in the sMAO–Cp$_2$ZrCl$_2$ system. We propose that complex activation results in a surface-supported [Cp$_8$ZrMe]$^+$ species, which is common to all catalysts with the same type of ancillary cyclpentadienyl ligands. Different Cp$_8$ ligand sets can result in over an order of magnitude difference in catalyst activity, and can produce different polymer properties.

By variation of the $\alpha$-donor (X) groups for simple sMAO–Cp$_2$ZrX$_2$ catalysts we observe smaller, but significant differences in polymerisation activity (ranging from 516 to 1160 kg PE mol$^{-1}$ h$^{-1}$), which is highest for the sMAO–Cp$_2$Zr(C$_6$F$_5$)$_2$ system. $^{19}$F NMR spectroscopy data for sMAO-Cp$_2$Zr(C$_6$F$_5$)$_2$ are consistent with C$_6$F$_5$ group transfer from Zr to Al during complex activation. Immobilisation of Cp$_2$ZrMe$_2$ on a C$_6$F$_5$ modified sMAO support, yields a catalyst system with very similar spectroscopic and polymerisation properties to those of sMAO-Cp$_2$Zr(C$_6$F$_5$)$_2$. This provides supporting evidence for a secondary interaction between the [Cp$_2$ZrMe]$^+$ species and the sMAO surface, which can influence catalytic activity. Further studies are needed to understand the nature of the interactions between the activator surface and the methylzirconocene species, to enable optimisation of both the solid support and complex in catalyst design.

Conflicts of interest

There are no conflicts to declare.

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