# Intercalation of catalytically active metal complexes in phyllosilicates and their application as propene polymerisation catalysts

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**The cationic Ziegler–Natta polymerisation catalyst $[Zr(\eta\text{-}C_5H_5Me(thf)]^+$, is intercalated in a synthetic fluorinated mica-type silicate ($NaMg_{2.5}Si_4O_{10}F_2$) and the modified, swelling synthetic hectorite [LaponiteRD, $Na_{0.46}Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}$], by ion-exchange of $[Zr(\eta\text{-}C_5H_5Me(thf)]^+$ ions with the interlamellar cations of the layered silicates; in the presence of methylalumoxane {MAO, $(MeAlO)_n$} these organometallic intercalation compounds are active catalysts for the polymerisation of propene giving low molecular mass atactic polypropylene with a narrow molecular mass distribution.**

Intercalation of inorganic or organic guests into lamellar inorganic matrices is now a widely studied reaction.[1] It provides synthetic chemists with low-temperature routes to modify either the structural, electronic or the chemical characteristics of the host matrix in a subtle and controllable manner. Layered aluminosilicates, in particular the charged 2:1 structures, possess diverse intercalation properties that have found a wide variety of applications including chemical catalysis and polymer nanocomposites.[2–6]

The ability of intercalation compounds to catalyse chemical reactions is not a widely investigated nor understood phenomenon. Pinnavaia and coworkers have reported a number of studies on selective catalytic hydrogenation of alkynes in which known homogeneous hydrogenation catalysts have been intercalated in a hectorite clay mineral.[6] The use of phyllosilicates as catalysts in organic chemistry is well documented and many studies on the shape selectivity of clay-supported catalysts for the hydrogenation of alkenes, alkynes, aldehydes and ketones and the asymmetric Diels–Alder reactions have been reported.[7–10] Prompted by these recent observations we were interested in finding methods of intercalating known homogeneous Ziegler–Natta alkene polymerisation catalysts into layered inorganic materials with a view to investigating their catalytic activity and selectivity.

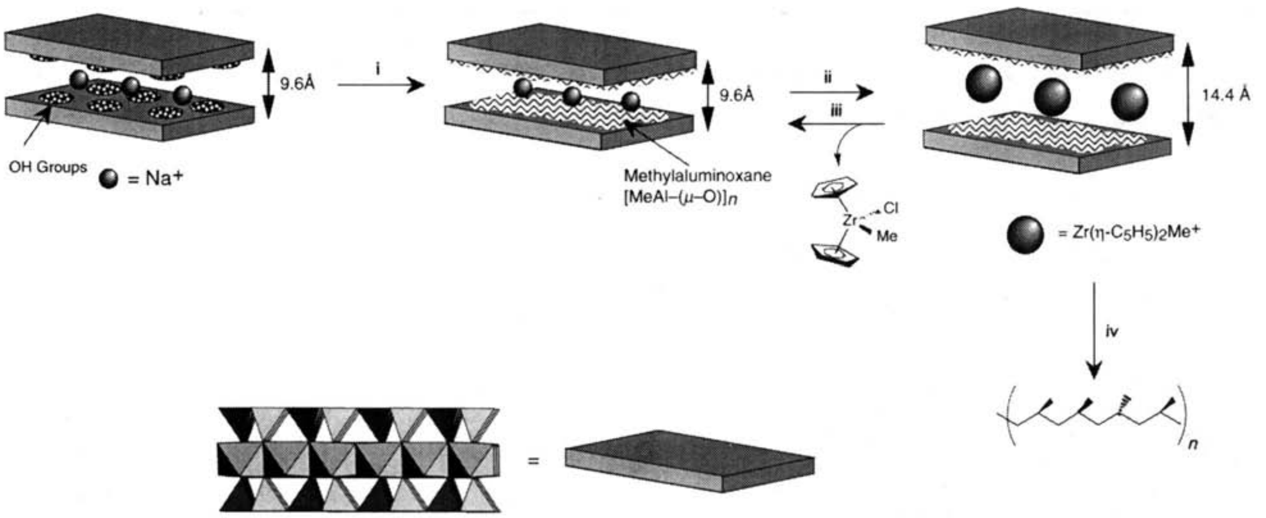
The last decade has seen major developments and understanding of homogenous Ziegler–Natta alkene polymerisation catalysis. The latest generation of catalysts based on modified bis(η-cyclopentadienyl)zirconium dichloride complexes in conjunction with the methylalumoxane cocatalyst are extremely active especially towards propene polymerisation and produce highly stereoregular isotactic polypropylene.[11,12] We were interested in discovering catalyst systems which could be intercalated into a layered host system so as to provide a way of modifying the activity and selectivity of these catalytically active centres.

We chose to investigate the potential of layered silicates as possible host lattices. These materials exhibit a wide diversity of intercalation reactions and also may themselves interact with the guest molecules to function as Lewis-acid cocatalyst.[13–15] Such a system where homogeneous reactions take place in a heterogenous framework may also have several advantages over the homogeneous analogues. This system may provide a strategy for alleviating the use of a vast excess of MAO, used in homogeneous systems, by reducing the Al:Zr ratio to a more tolerable and less costly level. Since the ion-exchanged materials contain no neutral zirconocene species, this ought to also limit the formation of stable, inactive dinuclear species which can lower the activity of many homogeneous catalysts.[16,17]

We have studied the intercalation of the homogeneous catalyst $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]^+$ into a number of layered silicates. We initially began by treating the synthetic smectite, LaponiteRD[‡], $[Na_{0.46}Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}]$ with MAO (Scheme 1) to remove all the acidic protons on the internal surfaces of the clay. Powder X-ray diffraction of the MAO-treated materials indicates almost no change in the interlayer separation but a slight loss of crystallinity as evidenced by the increase in the peak widths at half maximum (PWHM). Elemental microanalysis data indicated that the silicates typically contained *ca.* 16–20% by mass Al and the IR data also shows almost no residual absorptions assignable to Si–OH groups. The interlayer $Na^+$ ions can then be exchanged with $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]^+$ by treating the modified LaponiteRD with a solution of $[Zr(\eta\text{-}C_5H_5)_2(thf)]BPh_4$ in MeCN for 12 h. X-Ray powder diffraction shows that the interlayer spacing has expanded to 14.4 Å upon intercalation. The increase of the interlayer spacing ($\Delta c$ = 4.7 Å) is consistent with intercalation of the metallocene between the silicate layers. However, due to the almost spherical nature of the zirconocene cation we are unable to deduce any structural information on the nature or dynamics of these guest cations. The elemental microanalysis data suggest that essentially all the available $Na^+$ ions in the smectite are exchanged for the zirconocenium cation producing a material containing typically 0.37 mmol Zr (g silicate)$^{-1}$.[§] In the IR spectra, new bands are visible, assignable to $\nu(C_5H_5)$ bound to Zr. This zirconocene intercalated clay is extremely oxygen- and moisture-sensitive turning to a brown, catalytically inactive solid on exposure to air. The intercalated cations can recovered from the layers as $[Zr(\eta\text{-}C_5H_5)_2MeCl]$, by treatment of the intercalated silicate with an excess of NaCl.

Rather than chemically modify the internal surfaces on the clay as described above, we can also directly ion-exchange $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]^+$ into the synthetic fluorinated mica-type silicate (FTSM,[¶] $NaMg_{2.5}Si_4O_{10}F_2$). The FTSM is first heated under vacuum (150 °C at $4.5 \times 10^{-5}$ mbar) for 3 h; treatment of a suspension of the anhydrous fluorinated mica-type silicate with $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]BPh_4$ in MeCN for 12 h leads to an increase in the basal spacing of the host lattice from $c$ = 9.8 to 14.3 Å. Elemental microanalysis shows that this material contains 0.55 mmol Zr (g silicate)$^{-1}$. The intercalated cations can be exchanged out of the mica by reaction with thf solutions of NaCl giving $[Zr(\eta\text{-}C_5H_5)_2MeCl]$.

We have investigated the activity of both of these intercalated materials as propene polymerisation catalysts in the presence of MAO. The results for the polymerisation of propylene for both FTSM and the Laponite intercalated materials are outlined in Table 1. Supported catalysts were also produced to serve as a comparison for the intercalated materials. All polymerisation tests were carried out under the same conditions. The results indicate that both intercalated materials are remarkably active catalysts. Both materials give similar activities, $M_n$ and polydispersity values; being comparable to catalysts adsorbed



**Scheme 1** Schematic representation of the modification and ion-exchange of Laponite with $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]BPh_4$ and propene polymerisation. *Reagents and conditions*: i, MAO, toluene, 24 h, room temp.; ii, $[Zr(\eta\text{-}C_5H_5)Me(thf)]BPh_4$, MeCN, 12 h room temp.; iii, NaCl, thf, 12 h, room temp.; iv, propylene, 5 bar, 45 °C, toluene.

**Table 1** Propylene polymerisation activities and polymer properties[a]

| Material | Activity kg (mol Zr h)$^{-1}$ | $M_n$[b] GPC | Polydispersity |
|---|---|---|---|
| Intercalated materials | | | |
| Mica–$Zr(\eta\text{-}C_5H_5)_2Me^+$ | 1151 | 1846 | 1.9 |
| LaponiteRD–MAO–$Zr(\eta\text{-}C_5H_5)_2Me^+$ | 955 | 1996[c] | 2.4 |
| Supported materials | | | |
| LaponiteRD–MAO–$Zr(\eta\text{-}C_5H_5)_2Cl_2$ | 2325 | 1332[c] | 1.9 |
| Talc–MAO–$Zr(\eta\text{-}C_5H_5)_2Cl_2$ | 2174 | 1536 | 2.4 |
| Homogeneous analogues | | | |
| $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ | 1761 | 863[c] | 1.9 |
| $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]Bh_4$ | 2663 | 1516 | 1.8 |

[a] All reactions carried out with 5 bar propylene, at 40 °C with 250 ml toluene for a period of 30 min. A ratio of 1000 : 1 MAO : catalyst was used. [b] GPC *vs.* polystyrene. [c] Samples not fully soluble in thf so samples were filtered prior to analysis.

on silicate substrates. It is clearly important to distinguish between catalysis mediated by surface-bound zirconium species and the intercalated cations. Laponite has a cation exchange capacity (CEC) of 0.60 mequiv $g^{-1}$ and essentially all the available $Na^+$ ions are replaced by $Zr(\eta\text{-}C_5H_5)_2Me^+$, which accounts for almost all the zirconium found by elemental microanalysis; this implies that the amount of any surface absorbed zirconium species is negligible. For the FTSM (CEC = 0.94 mequiv. $g^{-1}$)[18] exchanged material, 68% of the exchangeable cations are replaced by the zirconocenium ions.

We have now demonstrated that highly reactive and catalytically active organometallic species can be intercalated in layered silicates. Initial studies have shown that they are active heterogeneous alkene polymerisation catalysts. These results open up the possibility of intercalating much more active and commercially important catalysts which may show possible selectivity.

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## Footnotes

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‡ Supplied by Laporte Absorbents Widnes, UK.

§ The elemental analysis of the $Zr(\eta\text{-}C_5H_5)_2Me^+$ intercalates varies with sample due to the varying extents of MAO reaction.

¶ Supplied by Topy Industries Tokyo, Japan.

‖ Corresponds to $Mg_{2.5}Si_4O_{10}F_2Na_{0.75\text{-}0.25}Zr(\eta\text{-}C_5H_5)Me(MeCN)$; Calc. (found): C 8.5(7.9), H 0.9(1.0), Zr 4.9(5.0)%.

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