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Ethylene Polymerisation using Solid Catalysts Based on Layered Double Hydroxides

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We report here the use of aluminoxane (MAO) modified Aqueous Miscible Organic Solvent Treated (AMOST) layered double hydroxide, $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ (AMO-Mg_3Al-CO_3) as a catalyst support system for the slurry phase polymerisation of ethylene using immobilised metallocene and non-metallocene metal complexes. The polymerisation data demonstrates that the catalyst productivity is dependent on the thermal treatment of the LDH and the temperature, pressure and time of the polymerisation. The solid catalyst system, AMO-Mg_3Al-CO_3/MAO/(^{Mes}PDI)$FeCl_2$ has been shown to have the highest overall activity for a non-metallocene system (14166 $kg_{PE}/mol_{complex}$/h/bar), and AMO-Mg_3Al-CO_3/MAO/($^{2\text{-Me},4\text{-Ph}}$SBI)$ZrCl_2$ was the most productive for a metallocene-based system (~3300 $kg_{PE}/mol_{complex}$/h/bar). The molecular weights and polydispersities vary with the complex on the AMO-LDH surface. Scanning electron microscopy images show that the morphology of the as produced polyethylene mimics that of the LDH support.

Introduction

Layered double hydroxides (LDHs) are a class of hydrotalcite-like clays with the general formula $[M^{z+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{y+}(X^{n-})_{y/n}$ (where commonly $z = 2$ and so $x = y$); known M^{2+} ions include Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} whilst M^{3+} ions include Sc^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+} and Al^{3+}.[1] LDHs have captured much attention in recent years due to their impact across a range of applications such as catalysis,[2,3] optics,[4] medical science,[5,6] and in inorganic-organic nanocomposites.[7-8] Recently, we have reported the synthesis of a new family of dispersible, hydrophobic LDHs using an aqueous miscible organic solvent treatment (AMOST) method. The AMO-LDHs produced by this method exhibit surface areas in excess of 400 m^2/g and pore volumes in excess of 2.15 cc/g, which is nearly two orders of magnitude higher than conventional layered double hydroxides.[9] AMO-LDHs have a unique chemical composition given by $[M^{z+}{}_{1-x}M'^{y+}{}_{x}(OH)_2]^{a+}(A^{n-})_{a/n}{\bullet}bH_2O{\bullet}c$(AMO-solvent), which instantly distinguishes them from conventional LDHs.[10]

Polyethylene is the most widely used polyolefin with a global production in 2011 of over 75 million tons per year, innovation in both the synthesis and the properties of polyethylene is still at the forefront in both industry and academia.[11] Many different supports (*e.g.* SiO_2, Al_2O_3, $MgCl_2$, and clays) and immobilisation procedures have been investigated.[12-15] He and Zhang reported the synthesis of LDH-polyethylene nanocomposites by in-situ polymerisation method using bis(4,4'-methylene-bis-(2,6-diisopropylimino))acenaphthene nickel dibromide complex.[16] Clays have been used as support for ethylene polymerisation using various catalytic systems based on zirconocene by Suga and co-workers.[17] Most commercial metallocene support systems strive to reproduce "single-centre" catalyst performance on systems based on porous spherical silica/aluminas.[18]

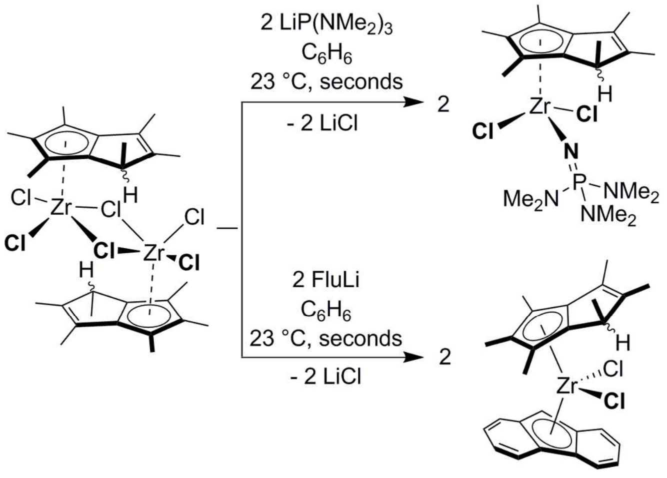
Very recently, we have reported the synthesis of metallocene supported on MAO-activated AMO-LDHs for the slurry phase polymerisation of ethylene. We demonstrated that the chemical composition of the specific AMO-LDH support can directly affect catalyst activity, polymer morphology, and polymer microstructure and that the AMO-LDHs afforded activities which were ten times higher than conventional-synthesised and commercial LDHs. A recent Zr K-edge EXAFS study of the active catalysts has enabled us to observe a metallocene derived single-centre catalytic species in close proximity to the LDH support.[19]

We report here the expansion of these studies focusing on the AMO-Mg_3Al-CO_3/MAO/complex solid catalyst system. We have investigated the effects of variation in thermal treatment of the LDH, catalyst loading and the metal complexes on the catalyst activity for polyethylene and properties of the polyethylene produced.

Results and discussion

Synthesis of new (hydro)permethylpentalene complexes

We recently demonstrated the synthesis and characterisation of new (hydro)permethylpentalene halide, alkoxide and aryloxide complexes for the polymerisation of polar monomers,[20] and permethylpentalene halide complexes for the polymerisation of ethylene in solution.[21] New complexes based on the (hydro)permethylpentalene ligand were synthesised by a straightforward salt metathesis route at 23 °C (Scheme 1). Reaction of $[Pn^*(H)ZrCl_3]_2$ with two equivalents of $LiNP(NMe_2)_3$ or FluLi resulted in the synthesis of $Pn^*(H)Zr\{NP(NMe_2)_3\}Cl_2$ and $Pn^*(H)(Flu)ZrCl_2$, respectively, in good yields. Group 4 phosphinimide complexes have been demonstrated to be extremely active for olefin polymerization.[48]



Scheme 1. Synthesis of new (hydro)permethylpentalene zirconium complexes.

Synthesis of the supported catalysts

All the supported catalysts used in this study were synthesised using acetone treated $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ LDH as the solid support, we have abbreviated this support to AMO-Mg_3Al-CO_3 using our previously reported naming procedure.[10]

Except when specified, the AMO-Mg_3Al-CO_3 was thermally treated at 150 °C for 6 h in a tube furnace under dynamic vacuum (1×10^{-2} mbar). Two equivalents of the thermally treated AMO-Mg_3Al-CO_3 was reacted with one equivalent of methylaluminoxane (MAO) in toluene at 80 °C for 2 h to give AMO-Mg_3Al-CO_3/MAO. Finally, one equivalent of the AMO-Mg_3Al-CO_3/MAO was reacted with 0.02 equivalents of the desired metal complex in toluene at 80 °C for 2 h to afford supported catalysts with the formula: **AMO-Mg_3Al-CO_3/MAO/complex**. A summary of all the metal complexes used in this study are collated in Fig. S1-S6. The previously reported complexes were either purchased or synthesised following literature procedures.[20-36] The X-ray powder diffraction data, IR spectra, SEM and TEM images, TGA and Solid state NMR data of a typical catalyst system; AMO-Mg_3Al-CO_3/MAO/complex are displayed in Fig. S7-S13.

The X-ray powder diffraction pattern for the thermally treated Mg_3Al-CO_3 AMO-LDH shows that it has lost both acetone and water and has begun changing into phase II (loss of Al-(OH)-Mg). An IR spectroscopic study of Mg_3Al-CO_3 AMO-LDH indicated two major characteristic absorptions: i) broad band with maximum at 3,400-3,680 cm^{-1} related to –OH stretching of layer double hydroxide as well as interlayer water and ii) strong absorption at approximately 1,350 cm^{-1} related to stretching mode of and CO_3^{2-} ion (Fig. S8a). IR spectrum of AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$ exhibited three noticeable characteristic peaks of methylaluminoxane (MAO) at 3,090, 3,020, and 2,950 cm^{-1} and the diminishing of –OH bending absorption of interlayer water at 1,650 cm^{-1}. Also, the results confirmed the remaining of hydroxyl group and anions in the layer structure of catalysts. It is possible to observe a Zr-C(*Me*) absorption around 800 cm^{-1} (Figure SI8b).

The thermal gravimetric analysis (TGA) of Mg_3Al-CO_3 AMO-LDH confirmed the loss of acetone and water but the materials maintains a layer structure at this temperature of thermal pre-treatment (150 °C), decomposition of the CO_3^{2-} anions occurs at around 260 °C.

We previously demonstrated that using a similar LDH that The surface area of AMO-LDH and AMO-LDH/MAO/(EBI)$ZrCl_2$ were found to be similar (101 and 114 m^2/g respectively) but the pore volume dramatically decreased (0.305 and 0.013 m^3/g) with the addition of methylaluminoxane and the complex.[19]

Solid state NMR spectroscopy observed features due to CO_3^{2-} ,methylaluminoxane and the complex in the AMO-Mg_3Al-CO_3/MAO/complex, Fig. S11.

The TEM and SEM images show that the initial LDH size for AMO-Mg_3Al-CO_3 LDH is around 10 μm, Fig. S12-S13.

Ethylene polymerisation - Thermal treatment of LDH support

We previously demonstrated that AMO-Mg_3Al-CO_3 was the most promising LDH support system due to its ease of synthesis, and its high catalytic activity and molecular weight of the polyethylene produced.[19]

To understand the effects of the thermal treatment of the LDH on the polymerisation activities; AMO-Mg_3Al-CO_3 LDH were thermally treated between 0 to 190 °C for 6 h, Fig. 1 and 2 and Table 1. Ethylene-bis(1-indenyl)zirconium dichloride, (EBI)$ZrCl_2$, and the bis(imino)pyridine iron complex, $(2,4,6\text{-}Me\text{-}C_6H_3N{=}CMe)_2C_5H_3N$, (^{Mes}PDI)$FeCl_2$, supported on AMO-$Mg_3Al$-$CO_3$/MAO were utilised during this study.

Table 1 Summary of the polymerisation of ethylene using different thermally treated AMO-Mg_3Al-CO_3. Supported catalyst = Mg_3Al -CO_3/MAO/complex

Temp (°C)	Complex	Activity[a]	M_w/M_n	M_w (g/mol)
0	(EBI)$ZrCl_2$	11	-	-
50	(EBI)$ZrCl_2$	17	7.31	590872
100	(EBI)$ZrCl_2$	514	3.81	264180
125	(EBI)$ZrCl_2$	1263	3.53	186306
150	(EBI)$ZrCl_2$	1276	4.08	194134
190	(EBI)$ZrCl_2$	394	-	-
0	(^{Mes}PDI)$FeCl_2$	75	22.11	344394
50	(^{Mes}PDI)$FeCl_2$	85	20.09	371823
100	(^{Mes}PDI)$FeCl_2$	2721	13.47	337626
125	(^{Mes}PDI)$FeCl_2$	4906	13.71	273078
150	(^{Mes}PDI)$FeCl_2$	6696	13.51	368083
190	(^{Mes}PDI)$FeCl_2$	5062	17.83	393204

[a] $kg_{PE}/mol_{complex}/h/bar$. Polymerisation conditions; 10 mg of catalyst, 2 bar, 1 hour, 60 °C, $[TIBA]_0/[M]_0 = 1000$, hexane (50 mL).

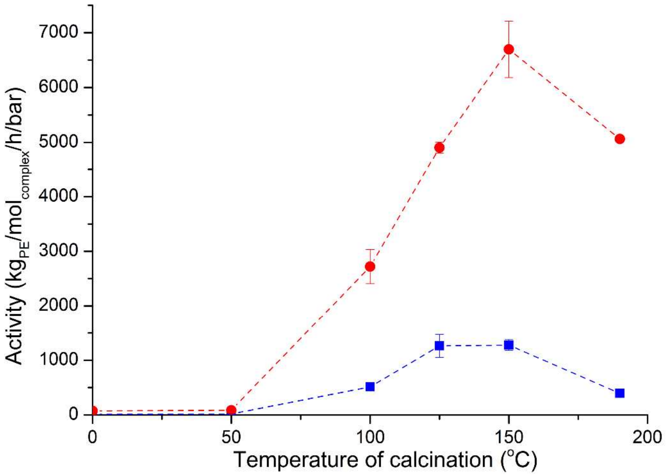


Fig. 1 Variation in ethylene polymerisation activities as a function of the thermal pretreatment temperature of AMO-Mg_3Al-CO_3. Supported catalyst = AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$ (blue square) and AMO-Mg_3Al-CO_3/MAO/(^{Mes}PDI)$FeCl_2$ (red circle). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, 60 °C, $[TIBA]_0/[M]_0 = 1000$, hexane (50 mL).

Using AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$, the thermal treatment range of 125-150 °C provided the highest activities (1263 and 1276 $kg_{PE}/mol_{complex}$/h/bar, respectively), Fig 1. Using (^{Mes}PDI)$FeCl_2$ as the supported complex, 150 °C was the temperature with the peak of activity (6696 $kg_{PE}/mol_{complex}$/h/bar). Remarkably, these values are higher than the solution polymerisation of ethylene reported by Brookhart and co-workers in the seminal work (values ~1250 $kg_{PE}/mol_{complex}$/h/bar at 60 °C).[15] Both catalysts demonstrate a dip in activity above 150 °C, certainly due to a reduction of the number of hydroxyl group on the surface and so possible complex aggreggation.[37] Lo and co-workers demonstrated that metallocene pre-catalysts supported on silicas dried at lower temperatures (T < 200 °C) afforded higher activities that at high temperature.[38]

Using both pre-catalysts, it appears that the polymerisation activities are very low when the LDH was thermally treated below 100 °C, certainly due to the high presence of intercalated water in the LDH starting material.

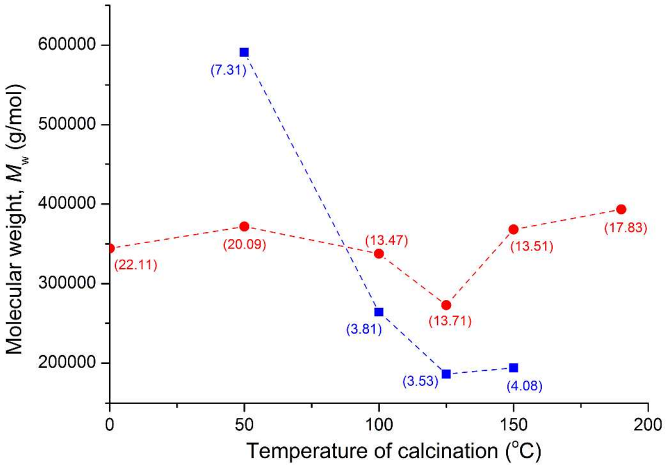


Fig. 2 Variation in polyethylene molecular weights (M_w) and polydispersities, (M_w/M_n) in parentheses as a function of the thermal pretreatment temperature of AMO-Mg_3Al-CO_3. Supported catalyst = AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$ (blue square) and AMO-Mg_3Al-CO_3/MAO/(^{Mes}PDI)$FeCl_2$ (red circle). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, 60 °C, $[TIBA]_0/[M]_0 = 1000$, hexane (50 mL).

The molecular weights vary as a function of the thermal pre-treatment temperature (0 to 190 °C) of the AMO-LDH. The molecular weights (M_w) of the polyethylene vary from 590872 to 194134 g/mol for AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$, and 344394 to 393204 g/mol for AMO-Mg_3Al-CO_3/MAO/(^{Mes}PDI)$FeCl_2$, Fig 2. The polydispersities when using the iron based pre-catalyst are very high ($M_w/M_w > 13.47$).

Ethylene polymerisation - Catalyst loading

After fixing on AMO-Mg_3Al-CO_3 thermally treated at 150 °C, we decided to study the effect of the amount of complex on the surface. We investigated the AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$ as the supported catalyst system with the AMO-Mg_3Al-CO_3/MAO:complex ratio between 100:1 – 100:4 at both 60 and 80 °C. The results are collated in Fig. 3 and 4, and Table 2.

Table 2. Summary of the polymerisation of ethylene using AMO-LDH/MAO/(EBI)$ZrCl_2$ with different catalyst loadings.

LDH/MAO: complex loading	T (°C)	Activity[a]	M_w/M_n	M_w (g/mol)
100:0	60	0	-	-
100:1	60	682	4.10	239015
100:2	60	1276	4.08	194134
100:3	60	1395	4.42	202726
100:4	60	590	4.02	223350
100:0	80	0	-	-
100:1	80	684	2.44	157004
100:2	80	1541	4.71	138340
100:3	80	1249	3.81	117050
100:4	80	713	3.91	135631

[a] $kg_{PE}/mol_{complex}$/h/bar. Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, $[TIBA]_0/[Zr]_0 = 1000$, hexane (50 mL).

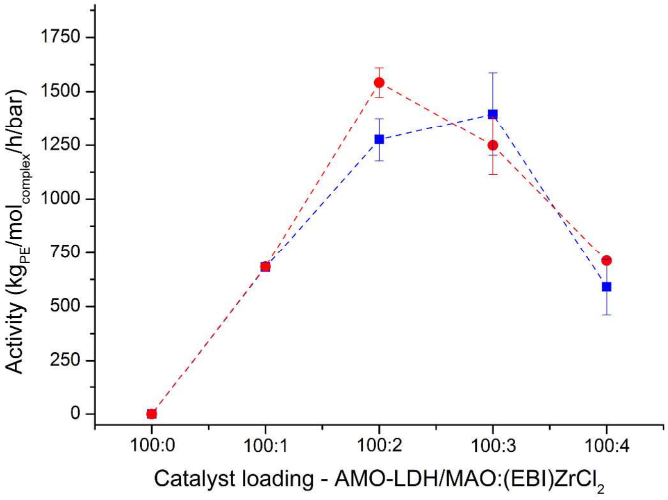


Fig. 3 Variation in ethylene polymerisation activity as a function of catalyst loading using AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$: 60 °C (blue square) and 80 °C (red circle). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, $[TIBA]_0/[M]_0 = 1000$, hexane (50 mL).

The weight ratio of AMO-Mg_3Al-CO_3/MAO:complex of 100:2 and 100:3 demonstrated the highest polymerisation activities at both 60 and 80 °C. Furthermore, when a weight pre-catalyst loading ratio of AMO-Mg_3Al-CO_3/MAO:(^{Mes}PDI)$FeCl_2$ of 100:3 was used at 60 °C, the activities was lower than when the ratio was 100:2 (4086 and 6696 $kg_{PE}/mol_{complex}$/h/bar respectively). These data show that above a certain catalyst loading the effectiveness of an individual catalytic site decreases.

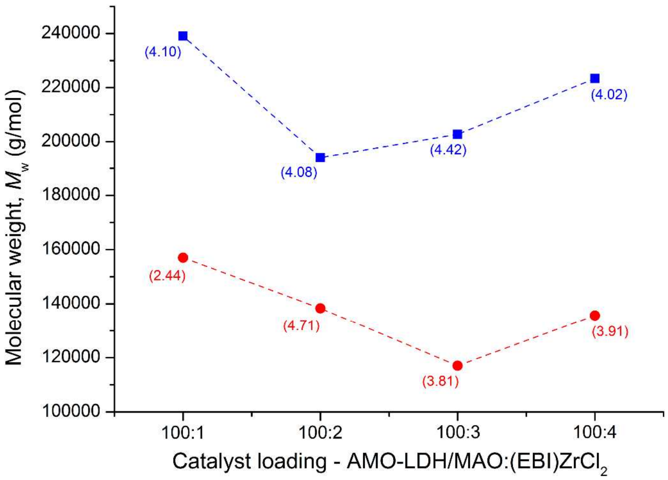


Fig. 4 Variation in polyethylene molecular weights (M_w) and polydispersities, (M_w/M_n) in parentheses as a function of (EBI)$ZrCl_2$ loading on AMO-Mg_3Al-CO_3/MAO/(EBI)$ZrCl_2$: 60 °C (blue square) and 80 °C (red circle). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, 60 °C, $[TIBA]_0/[M]_0 = 1000$, hexane (50 mL).

Fig. 4 shows that the molecular weights are all higher at 60 °C compared to 80 °C for any amount of (EBI)ZrCl$_2$ on the surface (M_w of 200000-240000 g/mol for 60 °C and 120000-155000 g/mol for 80 °C). This suggests that the termination rate increases faster relative to propagation rate as the molecular weight is determined by the ratio between the rates of propagation and termination. Hence, the molecular weights decreases with increase temperature as seen by Vollmer and co-workers.[39]

Ethylene polymerisation - Indenyl complexes

Following the study of the effects of thermal pretreatment and catalyst loading, it was decided to vary the metal complex on the AMO-Mg$_3$Al-CO$_3$/MAO. An overview of activities with the various complexes tested is displayed in Fig. S10.

The results of the polymerisation of ethylene using pre-catalysts based on metal indenyl complexes are displayed in Fig 5 and 6 and collated in Table 3.

Table 3 Summary of the polymerisation of ethylene using AMO-Mg$_3$Al-CO$_3$/MAO/complex with different indenyl based metal complexes.

Complex	T (°C)	Activity[a]	M_w/M_n	M_w (g/mol)
(EBI)ZrCl$_2$	60	1276	4.08	194134
(EBI)ZrCl$_2$	80	1542	4.71	138340
(SBI)ZrCl$_2$	60	539	4.31	278239
(SBI)ZrCl$_2$	80	1056	4.72	263365
(EBTHI)ZrCl$_2$	80	970	2.86	98641
($^{2\text{-Me},4\text{-Ph}}$SBI)ZrCl$_2$	60	3226	3.93	437490
($^{2\text{-Me},4\text{-Ph}}$SBI)ZrCl$_2$	80	3306	3.26	296346
(Ind)$_2$ZrCl$_2$	60	1470	3.16	188249
(Ind)$_2$ZrCl$_2$	80	488	2.95	145294

[a] kg$_{PE}$/mol$_{complex}$/h/bar. Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, [TIBA]$_0$/[Zr]$_0$ = 1000, hexane (50 mL).

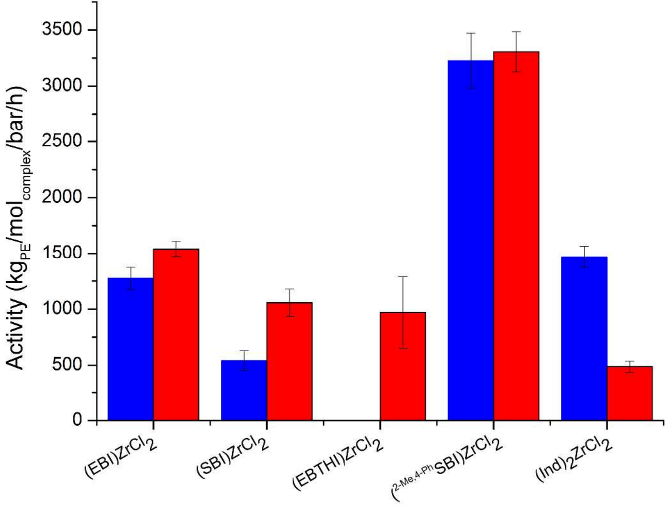


Fig. 5 Variation in polyethylene molecular weights (M_w) and polydispersities (M_w/M_n) using AMO-Mg$_3$Al-CO$_3$/MAO/complex: 60 °C (blue) and 80 °C (red). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, [TIBA]$_0$/[M]$_0$ = 1000, hexane (50 mL).

The metallocene catalyst, dimethylsilyl-bis{(2-methyl-4-phenyl(1-indene)} zirconium dichloride, ($^{2\text{-Me},4\text{-Ph}}$SBI)ZrCl$_2$, demonstrated the highest activities (~3300 kg$_{PE}$/mol$_{complex}$/h/bar) and the highest molecular weight (M_w of 437490 g/mol at 60 °C). Napoli and co-workers demonstrated that using ($^{2\text{-Me},4\text{-Ph}}$SBI)ZrCl$_2$ in solution ethylene polymerisation yielded an activity of 1185 kg$_{PE}$/mol$_{complex}$/h/bar and M_w of 7800 g/mol at 80 °C.[40] Similar finding were observed by Miri *et al.*.[41] Four catalysts demonstrated higher productivities at 80 °C; however, the catalyst based on bis(indenyl) zirconium dichloride, (Ind)$_2$ZrCl$_2$, had a activity three times higher at 60 °C than at 80 °C (1470 and 488 kg$_{PE}$/mol$_{complex}$/h/bar, respectively). The molecular weights for all catalyst systems are higher at 60 than 80 °C.[39] The change of the backbone of the complex on the surface from ethyl bridge, (EBI)ZrCl$_2$, to silyl, (SBI)ZrCl$_2$ decreased the activity at 60 and 80 °C (e.g. at 60 °C, activities of 1276 and 539 kg$_{PE}$/mol$_{complex}$/h/bar). However, the molecular weights are higher with the (SBI)ZrCl$_2$ based supported catalyst compared to (EBI)ZrCl$_2$ (at 60 °C, M_w of 278239 and 194134 g/mol respectively). Soga et al. reported the use of (SBI)ZrCl$_2$ in solution leading to activity of 19300 kg$_{PE}$/mol$_{complex}$/h.[42] When the (Ind)$_2$ZrCl$_2$ based supported catalyst was used, at 60 °C, the activity is similar than when bridged complexes, (EBI)ZrCl$_2$, were used on the surface but it is three times slower at 80 °C. Lee et al reported an activity of 400 kg$_{PE}$/mol$_{complex}$/h when trimethylaluminium treated silica supported (Ind)$_2$ZrCl$_2$ was used.[43] AMO-Mg$_3$Al-CO$_3$/MAO/(EBTHI)ZrCl$_2$ (where EBTHI is ethylene bis(1-tetrahydroindene) demonstrated the lowest molecular weight with M_w of 98641 g/mol and polydispersity (M_w/M_w of 2.86) but its activity was comparable to (EBI)ZrCl$_2$ based catalyst.

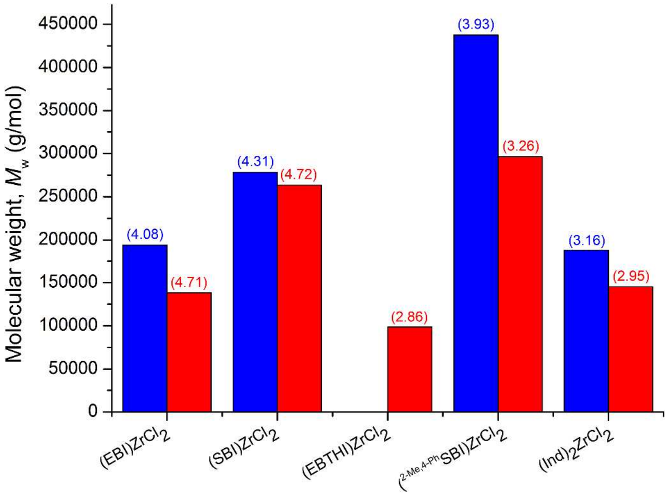


Fig. 6 Variation in polyethylene molecular weights (M_w) and polydispersities (M_w/M_n) parentheses using AMO-Mg$_3$Al-CO$_3$/MAO/complex: 60 °C (blue) and 80 °C (red). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, [TIBA]$_0$/[M]$_0$ = 1000, hexane (50 mL).

Ethylene polymerisation - Cyclopentadienyl complexes

The results of the polymerisation of ethylene using pre-catalysts based on immobilised cyclopentadienyl complexes are collated in Table 4 and displayed in Fig. 7-9. The temperature of polymerisation favoured by all the complexes is 60 °C. The pre-catalysts based on the complexes, bis(tetramethylcyclopentadienyl) zirconium dichloride, ($^{\text{Me}4}$Cp)$_2$ZrCl$_2$, and bis(n-butylcyclopentadienyl) zirconium dichloride, ($^{n\text{Bu}}$Cp)$_2$ZrCl$_2$, demonstrated the highest activities at 60 °C (2058 and 2141 kg$_{PE}$/mol$_{complex}$/h/bar respectively).

Table 4 Summary of the polymerisation of ethylene using AMO-LDH/MAO/complex with a range of cyclopentadienyl metal complexes.

complex	T (°C)	Activity[a]	M_w/M_n	M_w (g/mol)
(Cp)$_2$ZrCl$_2$	60	191	3.21	325593
(Cp)$_2$ZrCl$_2$	80	79	3.39	180768
($^{\text{Me}}$Cp)$_2$ZrCl$_2$	60	465	2.71	325446
($^{1,3\text{-Me}}$Cp)$_2$ZrCl$_2$	60	1048	2.69	308090
($^{1,3\text{-Me}}$Cp)$_2$ZrCl$_2$	80	567	3.81	215941

$(^{Me4}Cp)_2ZrCl_2$	60	2058	2.66	280817
$(Cp^*)_2ZrCl_2$	60	687	2.77	319175
$(Cp^*)_2ZrCl_2$	80	173	3.85	143358
$(Cp^*)ZrCl_3$	60	55	3.82	143358
$(^{1\text{-}Me,3\text{-}nBu}Cp)_2ZrCl_2$	60	1530	2.51	269665
$(^{1\text{-}Me,3\text{-}nBu}Cp)_2ZrCl_2$	80	763	2.85	128531
$(^{nBu}Cp)_2ZrCl_2$	60	2141	3.40	744533
$(^{nBu}Cp)_2ZrCl_2$	80	540	2.85	128531
$(^{nBu}Cp)_2HfCl_2$	60	535	2.76	571818
$(^{nBu}Cp)_2HfCl_2$	80	142	3.23	160769
$(^{tBu}Cp)_2HfCl_2$	60	55	4.77	679829
$(^{tBu}Cp)_2HfCl_2$	80	27	11.29	508554

[a] $kg_{PE}/mol_{complex}/h/bar$. Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, $[TIBA]_0/[Zr]_0 = 1000$, hexane (50 ml).

For cyclopentadienyl metal complexes immobilised on AMO-Mg_3Al-CO_3/MAO, there is an increase in activity with increasing number of methyl groups on the cyclopentadienyl ring up to four methyl groups then a drop for permethylcyclopentadienyl, activity of 191, 2058 and 687 $kg_{PE}/mol_{complex}/h/bar$ for bis(cyclopentadienyl) zirconium dichloride, $(Cp)_2ZrCl_2$, $(^{Me4}Cp)_2ZrCl_2$ and bis(pentamethylcyclopentadienyl) zirconium dichloride, $(Cp^*)_2ZrCl_2$ respectively, Fig. 7. However, it seems that there is no influence on the polyethylene molecular weights and polydispersities, Fig 9. The molecular weights, M_w, are around 300000 g/mol and polydispersities, M_w/M_n are low for a supported system (M_w/M_n below 3 for most cyclopentadienyl based pre-catalysts). Coville and co-workers demonstrated a strong effect due to steric effect in cyclopentadienyl based zirconocene systems.[44] There is a strong effect on the activities, and over the control of the polymer properties with the addition of an extra cyclopentadienyl group from AMO-Mg_3Al-CO_3/MAO/$(Cp^*)ZrCl_3$ to the $(Cp^*)_2ZrCl_2$ analogue; the activity increased by twelve fold from 55 to 687 $kg_{PE}/mol_{complex}/h/bar$, the molecular weights increased from 143358 to 319175 g/mol and the polydispersities decreased from 3.82 to 2.77, Fig. 7. These data demonstrate a better control of the ethylene polymerisation. Numerous reports have been published reporting the polymerisation activity of bis(cyclopentadienyl) zirconium dichloride on solid supports from none to 10000 $kg_{PE}/mol_{complex}/h$ (when polymethylaluminoxane was used as co-catalyst) and molecular weights varying from 50000 to 30000 g/mol.[45]

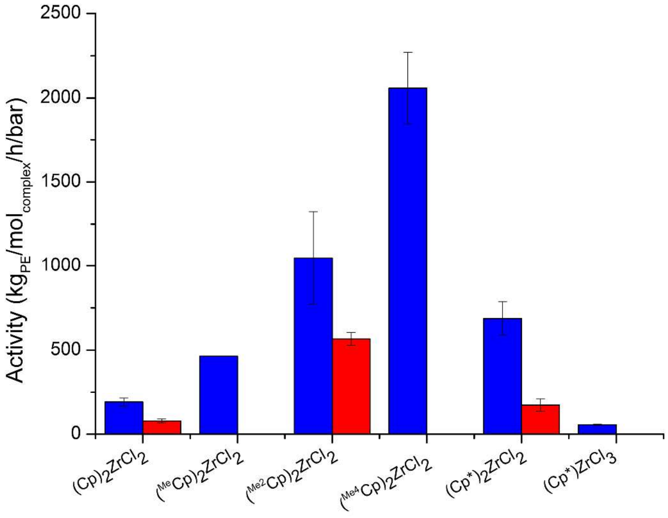


Fig. 7 Variation in ethylene polymerisation activities using AMO-Mg_3Al-CO_3/MAO/complex: 60 °C (blue) and 80 °C (red). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, $[TIBA]_0/[M]_0 = 1000$, hexane (50 mL).

Using hafnium based supported catalysts at 60 °C, the complex $(^{nBu}Cp)_2HfCl_2$ shows an activity ten times higher than the *tert*-butyl analogue $(^{tBu}Cp)_2HfCl_2$ (535 and 55 $kg_{PE}/mol_{complex}/h/bar$ respectively), Fig. 8. However, it is still five times slower than that of its zirconium congener based on $(^{nBu}Cp)_2ZrCl_2$ with an activity of 2141 $kg_{PE}/mol_{complex}/h/bar$, Fig. 8. The change of the alkyl group from methyl to *n*-butyl increased the activity by a factor of five (465 and 2141 $kg_{PE}/mol_{complex}/h/bar$) and the molecular weight by a factor of two (325446 and 744533 g/mol) for $(^{Me}Cp)_2ZrCl_2$ and $(^{nBu}Cp)_2ZrCl_2$ based supported catalysts respectively, Table 4. Similarly, Lee and co-workers demonstrated a factor of two in increase of the activity (1000 to 2007 $kg_{PE}/mol_{complex}/h$).[43]

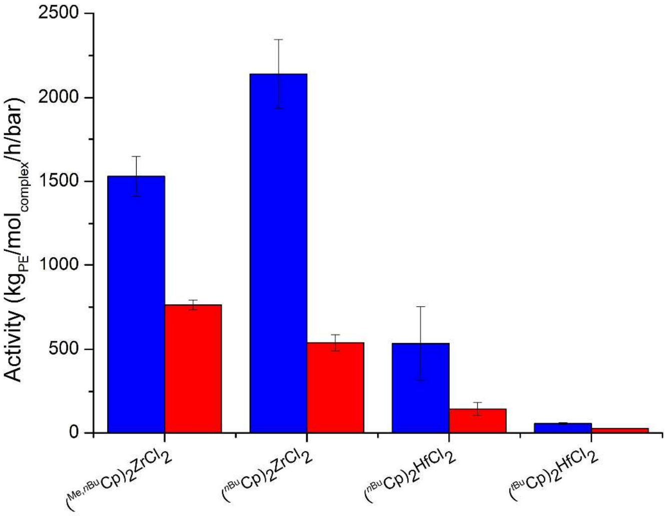


Fig. 8 Variation in ethylene polymerisation activities using AMO-Mg_3Al-CO_3 /MAO/complex: 60 °C (blue) and 80 °C (red). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, $[TIBA]_0/[M]_0 = 1000$, hexane (50 mL).

Except when AMO-Mg_3Al-CO_3/MAO/$(^{tBu}Cp)_2HfCl_2$ was used, all polydispersities, M_w/M_w, were below 4. The molecular weights of were very high at 60 °C (M_w up to 744,533 g/mol for AMO-Mg_3Al-CO_3/MAO/$(^{nBu}Cp)_2ZrCl_2$. Fig 9. These molecular weights are similar than those reported by Kaminsky and co-workers (50000 to 600000 g/mol).[46]

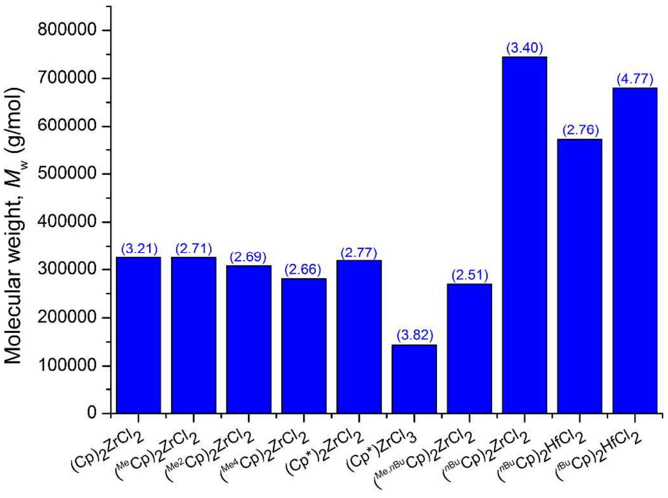


Fig. 9 Variation in polyethylene molecular weight (M_w), and polydispersities, (M_w/M_n) using AMO-Mg_3Al-CO_3/MAO/complex. Polymerisation conditions:

10 mg of pre-catalyst, 2 bar, 1 hour, $[\text{TIBA}]_0/[\text{M}]_0 = 1000$, 60 °C, hexane (50 mL).

Ethylene polymerisation – Permethylpentalenyl and (hydro)permethylpentalenyl complexes

The results of the polymerisation of ethylene using various pre-catalysts based on permethylpentalenyl and (hydro)permethylpentalenyl complexes are collated in Table 5. At 80 °C, $\text{Pn}^*(\text{H})\text{ZrCl}_2(\text{Flu})$, demonstrated an activity four times higher than the phosphine-imido, $\text{Pn}^*(\text{H})\text{ZrCl}_2\text{P}(\text{NMe}_2)_3$ pre-catalyst (122 and 34 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$ respectively). All the molecular weights and polydispersities are very high at 60 and 80 °C (M_w up to 824999g/mol and M_w/M_n up to 37.68)

The (hydro)permethylpentalenyl complex, $[\text{Pn}^*(\text{H})\text{ZrCl}_3]_2$, polymerise ethylene four times faster than the non-hydrogenated, $[(\text{Pn}^*)\text{ZrCl}_2]_2$, activity of 89 and 24 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$ respectively.

Table 5 Summary of the polymerisation of ethylene using AMO-Mg_3Al-CO_3/MAO/complex using a range of immobilised (hydro)permethylpentalenyl and permethylpentalenyl metal complexes.

Complex	T (°C)	Activity[a]	M_w/M_n	M_w (g/mol)
$[(\text{Pn}^*)\text{ZrCl}_2]_2$	80	24	7.49	824999
$[\text{Pn}^*(\text{H})\text{ZrCl}_3]_2$	80	89	23.54	854491
$\text{Pn}^*(\text{H})\text{ZrCl}_2\text{NP}(\text{NMe}_2)_3$	60	57	6.56	416854
$\text{Pn}^*(\text{H})\text{ZrCl}_2\text{NP}(\text{NMe}_2)_3$	80	34	3.07	120612
$\text{Pn}^*(\text{H})\text{ZrCl}_2(\text{Flu})$	60	213	37.68	730214
$\text{Pn}^*(\text{H})\text{ZrCl}_2(\text{Flu})$	80	122	25.09	483584

[a] $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$. Polymerisation conditions: $\text{Mg}_3\text{Al-CO}_3$, 10 mg of pre-catalyst, 2 bar, 1 hour, $[\text{TIBA}]_0/[\text{Zr}]_0 = 1000$, hexane (50 ml).

Ethylene polymerisation – Non-metallocene complexes

The results of the polymerisation of ethylene using a AMO-Mg_3Al-CO_3/MAO/non-metallocene solid catalyst in which the immobilised metal complex is a range of non-metallocene metal complexes are collated in Table 6. The complexes used were bis(imino)pyridine iron complex, $(^{\text{Mes}}\text{PDI})\text{FeCl}_2$,[47] (ArN=C(R)C(R)=NAr)$\text{NiBr}_2$ (Ar = 2,6-^{i}Pr-C_6H_3 and R = C_6H_6), $(^{2,6\text{-iPr-Ph}}\text{DI})\text{NiBr}_2$,[26,29] (ArN=C(R)C(R)=NAr)PdClMe (Ar = 2,6-Me-C_6H_3 and R = C_6H_6), $(^{2,6\text{-Me-Ph}}\text{NDI})\text{PdClMe}$,[28,29] permethylcyclopentadienyl titanium dichloride phosphinimide, $(\text{Cp}^*)\text{TiCl}_2(\text{N}\{\text{P}^t\text{Bu}\}_3)$,[48] constrained geometry catalyst (CGC), $(^{\text{Me4}}\text{Cp})\text{Me}_2\text{SiN}(^t\text{Bu})\text{TiCl}_2$,[49] and $\{\eta^2$-1-[C(H)=NR]-2-O-3-^{t}Bu-$\text{C}_6\text{H}_3\}_2$ (where R = 2,3,4,5,6-pentafluorophenyl group 4 dichloride, $(^{\text{ArF}}{}_5\text{FI})\text{MCl}_2$ (where M = Zr or Ti).[34]

Table 6 Summary of the polymerisation of ethylene using AMO-Mg_3Al-CO_3/MAO/complex catalyst using a range of immobilised non-metallocene metal complexes.

Complex	Temp (°C)	Activity[a]	M_w/M_n	M_w (g/mol)
$(^{2,6\text{-iPr-Ph}}\text{DI})\text{NiBr}_2$	60	47	5.57	694096
$(^{2,6\text{-iPr-Ph}}\text{DI})\text{NiBr}_2$	80	14	-	-
$(^{\text{Me4}}\text{Cp})\text{Me}_2\text{SiN}(^t\text{Bu})\text{TiCl}_2$	60	243	4.26	1032406
$(^{\text{Me4}}\text{Cp})\text{Me}_2\text{SiN}(^t\text{Bu})\text{TiCl}_2$	80	157	7.30	862218
$(\text{Cp}^*)\text{TiCl}_2(\text{N}\{\text{P}^t\text{Bu}\}_3)$	60	3549	2.51	269665
$(\text{Cp}^*)\text{TiCl}_2(\text{N}\{\text{P}^t\text{Bu}\}_3)$	80	3281	2.57	160260
$(^{\text{Mes}}\text{PDI})\text{FeCl}_2$	60	6696	13.51	368083
$(^{\text{Mes}}\text{PDI})\text{FeCl}_2$	70	5500	14.32	251468
$(^{\text{Mes}}\text{PDI})\text{FeCl}_2$	80	3713	14.58	202503
$(^{2,6\text{-Me-Ph}}\text{NDI})\text{PdClMe}$	60	20	-	-
$(^{\text{ArF}}{}_5\text{FI})\text{ZrCl}_2$	60	2479	7.03	448022
$(^{\text{ArF}}{}_5\text{FI})\text{TiCl}_2$	60	75	-	-

[a] $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$. Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, $[\text{TIBA}]_0/[\text{M}]_0 = 1000$, hexane (50 ml).

At 60 °C, bis(imino)pyridine iron complex, $(^{\text{Mes}}\text{PDI})\text{FeCl}_2$, demonstrated the highest activity of all the complexes (6696 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$) followed by $(\text{Cp}^*)\text{TiCl}_2(\text{N}\{\text{P}^t\text{Bu}\}_3)$ and $(^{\text{ArF}}{}_5\text{FI})\text{ZrCl}_2$ (activities of 3549 and 2479 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$ respectively) demonstrating very high activity on the Gibson's scale, Table 6. These complexes have already shown in the literature to yield very high activity.[34,47,48] Gibson and co-workers demonstrated an activity of 305 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$ and Mw of 132000 g/mol using $(^{\text{Mes}}\text{PDI})\text{FeCl}_2$.[47] The zirconium phenoxy-imine, $(^{\text{ArF}}{}_5\text{FI})\text{ZrCl}_2$, was 33 times faster the titanium analogous (2479 and 75 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$) which is the opposite trend that the one reported by Fujita and co-workers. The constrained geometry based supported catalyst afforded very low activities, below 300 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$, certainly due to its immobilisation on LDHs. The highest molecular weights were achieved using AMO-Mg_3Al-CO_3/MAO/$(\text{Cp}^*)\text{TiCl}_2(\text{N}\{\text{P}^t\text{Bu}\}_3)$ as a catalyst (M_w of 1032406 g/mol at 60 °C with a polydispersity, M_w/M_n, of 4.26).

Fig. 10 displayed the results using AMO-Mg_3Al-CO_3/MAO/$(^{\text{Mes}}\text{PDI})\text{FeCl}_2$. Both activities and molecular weights decreased with increasing temperature from 60 to 80 °C (from 6696 to 3713 $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$ and from 368083 to 202503 g/mol respectively). However, the catalyst demonstrated very poor control over the polymer morphology with polydispersities above 13.51, Fig. 10.

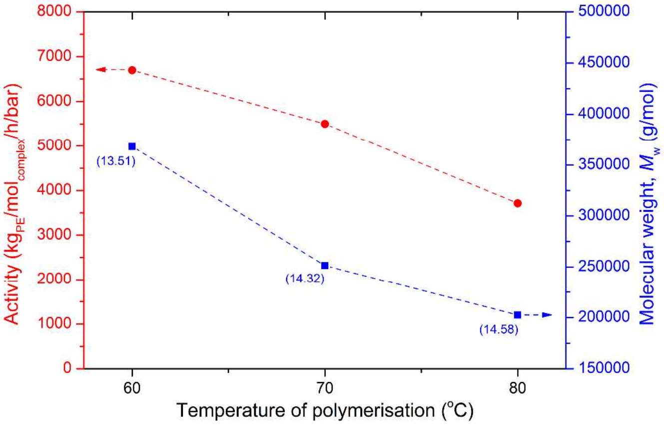


Fig. 10 Variation in ethylene polymerisation activities and molecular weights *vs.* temperature of polymerisation using AMO--CO_3/MAO/$(^{\text{Mes}}\text{PDI})\text{FeCl}_2$: M_w (blue square) and activities (red circle). Polymerisation conditions: 10 mg of pre-catalyst, 2 bar, 1 hour, $[\text{TIBA}]_0/[\text{M}]_0 = 1000$, hexane (50 mL).

Ethylene polymerisation - Scale-up

The results of the polymerisation of ethylene using AMO-Mg_3Al-CO_3/MAO/complex solid catalysts in a 2 L steel reactor are collated in Table 7. The ethylene polymerisations were carried out at 8 bar, $[\text{TIBA}]_0/[\text{M}]_0 = 300$, hexane (1000 mL).

Table 7 Summary of the polymerisation of ethylene using AMO-Mg_3Al-CO_3/MAO/complex in large 2 L steel reactor.

Complex	T (°C)	Activity[a]	M_w/M_n	M_w (g/mol)
$(^{\text{Mes}}\text{PDI})\text{FeCl}_2$	70	14166	22.62	516145
$(^{2\text{-Me},4\text{-Ph}}\text{SBI})\text{ZrCl}_2$	70	2948	3.65	567861
$(^{n\text{Bu}}\text{Cp})_2\text{ZrCl}_2$	70	9838	2.30	162437
$(\text{Cp}^*)\text{TiCl}_2(\text{N}\{\text{P}^t\text{Bu}\}_3)$	70	1000	-	-

[a] $\text{kg}_{\text{PE}}/\text{mol}_{\text{complex}}/\text{h}/\text{bar}$ bar. Polymerisation conditions: $\text{Mg}_3\text{Al-CO}_3$, 100 mg of pre-catalyst, 8 bar, 1 hour, $[\text{TIBA}]_0/[\text{Zr}]_0 = 300$, hexane (1000 mL).

As previously shown in the ethylene polymerisation carried out in ampoules at 2 bar, with the supported catalyst AMO-LDH/MAO/(^{Mes}PDI)FeCl$_2$ has the highest activity with 14166 kg$_{PE}$/mol$_{complex}$/h/bar, three times the value obtained at 2 bar (5500 kg$_{PE}$/mol$_{complex}$/h/bar). This is followed by the supported catalyst based on ($^{n\text{Bu}}$Cp)$_2$ZrCl$_2$ with an activity of 9838 kg$_{PE}$/mol$_{complex}$/h. The molecular weights are three times higher for iron based catalyst than the zirconium one (M_w of 516145 and 162437 g/mol respectively) but the polydispersity is far higher (M_w/M_n of 22.62 and 2.30 respectively). Hydrogen feed was added to the reactor in an attempt to control the molecular weights. At 70 °C, using 50 mg of catalyst AMO-Mg$_3$Al-CO$_3$/MAO/(^{Mes}PDI)FeCl$_2$, activities of 15572 and 20940 kg$_{PE}$/mol$_{complex}$/h/bar were obtained in the absence and presence of hydrogen respectively, demonstrating an increasing of activity of 30% with the presence of hydrogen. However, the molecular weights and polydispersities are similar (M_w of 541149 and 535076 g/mol, and M_w/M_n of 24.16 and 23.60, respectively). In contrast to the polymerisation in ampoules, AMO-Mg$_3$Al-CO$_3$/MAO/($^{2\text{-Me,4-Ph}}$SBI)ZrCl$_2$ demonstrated very low activity despite varying the time, temperature and the addition of hydrogen. Fig. S11 highlights the ethylene intake by the four catalysts demonstrating a strong intake then a slow decrease for AMO-Mg$_3$Al-CO$_3$/MAO/(^{Mes}PDI)FeCl$_2$ and AMO-Mg$_3$Al-CO$_3$/MAO/($^{n\text{Bu}}$Cp)$_2$ZrCl$_2$.

The polyethylene synthesised using the zirconocene based pre-catalysts demonstrated larger sized particles with 60 and 72% of particles diameter above 250 µm for AMO-Mg$_3$Al-CO$_3$/MAO/($^{n\text{Bu}}$Cp)$_2$ZrCl$_2$ and AMO-LDH/MAO/($^{2\text{-Me,4-Ph}}$SBI)ZrCl$_2$ respectively (Fig. 11).

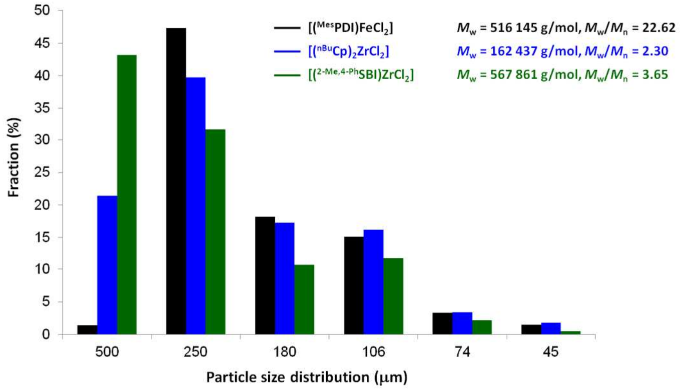


Fig. 11 Polyethylene particle size distribution using AMO-Mg$_3$AlCO$_3$ /MAO/complex. Pre-catalyst conditions: Mg$_3$Al-CO$_3$, 100 mg of pre-catalyst, 1 hour, 8 bar, [TIBA]$_0$/[M]$_0$ = 300, hexane (1000 mL).

The SEM pictures of the polyethylene synthesised using AMO-Mg$_3$AlCO$_3$/MAO/complex are shown Fig. 12-13 and in Fig. SI14-16.

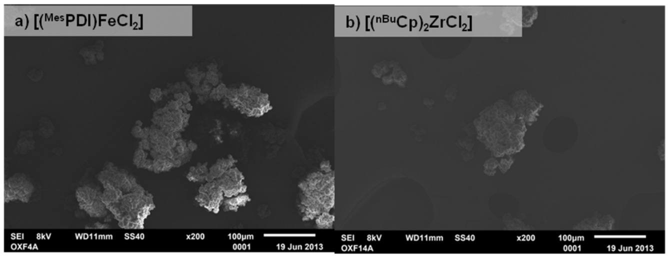


Fig. 12 SEM image of polyethylene using AMO-Mg$_3$AlCO$_3$/MAO/complex. Catalyst conditions: Mg$_3$Al-CO$_3$, 10 mg of catalyst, 2 bar, 1 hour, [TIBA]$_0$/[M]$_0$ = 1000, hexane (50 mL), a) (^{Mes}PDI)FeCl$_2$ and b) ($^{n\text{Bu}}$Cp)$_2$ZrCl$_2$.

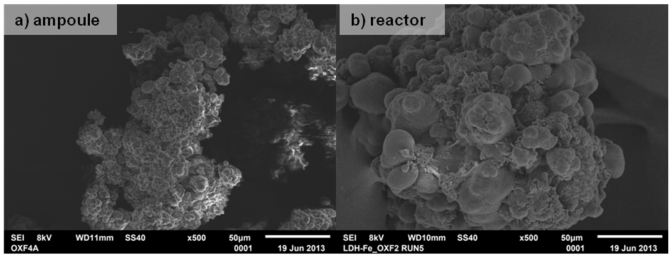


Fig. 13 SEM image of polyethylene using AMO-Mg$_3$AlCO$_3$ /MAO/(^{Mes}PDI)FeCl$_2$. Catalyst conditions: (a) Mg$_3$Al-CO$_3$, 10 mg of catalyst, 2 bar, 1 hour, [TIBA]$_0$/[M]$_0$ = 1000, hexane (50 mL), and (b) Mg$_3$Al-CO$_3$, 100 mg of catalyst, 8 bar, 1 hour, [TIBA]$_0$/[M]$_0$ = 300, hexane (1000 mL).

The polyethylene particle morphology mimics the LDH support for AMO-Mg$_3$Al-CO$_3$/MAO/(^{Mes}PDI)FeCl$_2$ and AMO-Mg$_3$Al-CO$_3$/MAO/($^{n\text{Bu}}$Cp)$_2$ZrCl$_2$ obtained when the polymerisations were carried out in ampoules at 2 bar pressure, Fig. 13. The morphology is different when the polymerisations were carried out in a steel reactor at 8 bar pressure, the particles are bigger, Fig. 14.

Experimental Details

Synthesis of Pn*(H)Zr{NP(NMe$_2$)$_3$}

To a solution of [Pn*(H)ZrCl$_3$]$_2$ (0.290 g, 0.376 mmol) in benzene (2 mL) was added a slurry of LiNP(NMe$_2$)$_3$ (0.139 g, 0.752 mmol) to afford an orange solution and colourless precipitate. The reaction mixture was stirred for 1 h before the solution was filtered. The filtrate was dried *in vacuo* to yield Pn*(H)Zr{NP(NMe$_2$)$_3$}Cl$_2$ as an orange solid. Yield: 0.142 g (72%). ^{1}H NMR (benzene-d_6, 23 °C): δ 3.68 (q, 1H, $^3J_{HH}$ = 7.5 Hz, Pn*(*H*)), 2.35 (d, 18 H, $^3J_{PH}$ = 10.0 Hz, NMe$_2$), 2.34 2.27 2.24 2.12 1.78 (s, 3H each, C*H$_3$*-Pn*(H)), 1.23 (d, 3H, $^3J_{HH}$ = 7.5 Hz, 1-C*H$_3$*-Pn*(H)). ^{13}C{^{1}H} NMR (benzene-d_6, 23°C): δ 144.5 138.3 135.1 128.8 124.9 118.9 113.8 (*q*-Pn*(H)), 45.0 (1-Pn*(H)), 37.2 (d, $^3J_{PC}$ = 3.6 Hz, NMe$_2$), 16.2 (1-*C*H$_3$-Pn*(H)), 12.7, 12.3, 12.3, 12.2 12.1 (*C*H$_3$-Pn*(H)).

Synthesis of Pn*(H)(Flu)ZrCl$_2$

To a mixture of [Pn*(H)ZrCl$_3$]$_2$ (0.212 g, 0.276 mmol) and FluLi (0.0951 g, 0.551 mmol) was added benzene (5 mL) to afford a pale yellow solution and colourless precipitate. The reaction mixture was filtered and the filtrate dried *in vacuo* to yield Pn*(H)(Flu)ZrCl$_2$ as a pale yellow solid. Yield: 0.108 g (76%). A 50:50 mixture of diastereomers was obtained as judged by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy; many resonances are overlapping or closely spaces; all are listed for completeness. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.25 (m, 4H, C$_6$H$_4$), 7.18 – 7.14 (m, 2 H, C$_6$H$_4$), 7.07 (m, 2 H, C$_6$H$_4$), 5.49 (m, 1H, Flu-*H*), 3.18 (m, 1 H, Pn*(*H*)), 2.17 2.12 2.11 2.09 2.02 2.02 1.90 1.86 1.68 1.68 (s, 3H each, C*H$_3$*-Pn*(H)), 1.13 1.09 (d, 3H each, $^3J_{HH}$ = 7.4 Hz, 1-C*H$_3$*-Pn*(H)). ^{13}C{^{1}H} NMR (benzene-d_6, 23°C): δ 148.5 (C$_6$H$_4$), 144.7 1.44.4 138.5 138.2 136.4 136.1 128.6 128.6 (*q*-Pn*(H)), 126.8 (C$_6$H$_4$), 126.3 126.1 (*q*-Pn*(H)), 125.8 125.8 (C$_6$H$_4$), 119.1 119.0 114.5 114.3 (*q*-Pn*(H)), 81.0 (Flu-H), 43.7 43.6 (1-Pn*(H)), 28.1 28.0, 15.9 15.8 (1-*C*H$_3$-Pn*(H)), 12.5 12.2 12.0 11.9 11.9 11.6 11.5 (*C*H$_3$-Pn*(H)).

Synthesis of previously reported complexes. The complexes used in this study which were previously reported have been purchased or synthesised via modified literature procedures,[22-36] their syntheses are reported in the supporting information. [(Pn*H)ZrCl$_3$]$_2$, and [Pn*(H)ZrCl$_3$]$_2$ have been recently reported.[20a,20b]

Synthesis of AMO-Mg_3AlCO_3. $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ (AMO-Mg_3AlCO_3) was synthesised using a method adapted from the literature.[11,12a] $Mg(NO_3)_2{\cdot}6H_2O$ (9.60 g, 37.4 mmol) and $Al(NO_3)_3{\cdot}9H2O$ (4.68 g, 12.5 mmol) were dissolved in 50 mL distilled water (Solution A). A second solution was made using Na_2CO_3 (2.65 g, 25.0 mmol) dissolved in 50 mL distilled water and made to pH 10 by the addition of approximately 5 mL of 1M HNO_3 (Solution B). Solution A was added to Solution B dropwise over 30 minutes with stirring with the pH maintained at pH 10 using 1M NaOH. The resulting solution was stirred for 16 hours. Then, the LDH slurry was washed with distilled water at 70 °C until the pH of the washings was pH 7. The slurry was then washed with 200 mL of acetone and then dispersed in 200 mL of acetone for one hour. This washing and dispersion process was repeated on the slurry three times. After washing, the slurry was dried for 24 hours in a vacuum oven at 60 °C.

Synthesis of the supported catalysts. Synthesised AMO-Mg_3AlCO_3 was thermally treated at 150 °C for 6 h under $1\text{x}10^{-2}$ mbar and then kept under nitrogen atmosphere. Thermally treated LDH was weighed and slurried in toluene. Methylaluminoxane (MAO) with MAO:LDH weight ratio of 0.4 was prepared in toluene solution and added to the thermally treated LDH toluene slurry. The resulting slurry was heated at 80 °C for 2 h with occasional swirling (not stirring was used to avoid gridding of the support). The product was then filtered, washed with toluene, and dried under dynamic vacuum to afford AMO-Mg_3Al-CO_3/MAO support. AMO-Mg_3Al-CO_3/MAO support was weighed and slurried in toluene. A solution of complex in toluene with AMO-Mg_3Al-CO_3/MAO support: catalyst weight ratio of 0.02 was prepared and added to the AMO-Mg_3Al-CO_3/MAO slurry. The resulting slurry was heated at 60 °C for 1 h with occasional swirling (not stirring was used to avoid gridding of the support) or until the solution became colourless. The product was then filtered and dried under dynamic vacuum to afford complex supported AMO-Mg_3Al-CO_3/MAO pre-catalyst. Another technique of immobilisation used was to introduce both the AMO-Mg_3Al-CO_3/MAO and (EBI)$ZrCl_2$ solids in the same Schlenk , then to add toluene unto them; work-up as before. Both techniques demonstrated similar polymerisation activities.

Ethylene polymerisation. The complex supported AMO-Mg_3Al-CO_3/MAO pre-catalyst and TIBA were weighed with the desired ratio and put together in a Rotaflo ampoule. Hexane was added to the mixture. Ethylene gas was fed to start the polymerisation at the targeted temperature. After the desired time, the reaction was stopped, the polymer was quickly filtered and washed with pentane (2 × 25 mL). The polymer was dried in vacuum oven at 55 °C. The tests were repeated at least twice for each individual set of polymerisation conditions.

Conclusions

We have reported a detailed study of the use of an aluminoxane (MAO) modified Aqueous Miscible Organic Solvent Treated layered double hydroxide, $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ (AMO-Mg_3Al-CO_3) as a solid support for the immobilisation of metallocene and non-metallocene metal complexes and their use as solid catalysts in the slurry polymerisation of ethylene. The polymerisation data demonstrated that catalyst activity is dependent on a range of parameters such as thermal treatment, catalyst loading, and polymerisation temperature. The thermal pretreatment AMO-LDH was found to be very important feature to control polymerisation activity, pretreatment at 150 °C produces the highest activity for (EBI)$ZrCl_2$ and (^{Mes}PDI)$FeCl_2$ supported catalysts. The catalyst loading was found to be optimal for a support:complex ratio of 100:2.

The AMO-Mg_3Al-CO_3/MAO/(^{Mes}PDI)$FeCl_2$ was shown to have the highest overall catalytic activity and AMO-Mg_3Al-CO_3/MAO/($^{2\text{-Me},4\text{-Ph}}$SBI)$ZrCl_2$ was the most active catalyst suing a metallocene-type complex. The molecular weights and polydispersities vary with nature of the supported complex. For supported cyclopentadienyl metal complexes the activity of the catalyst system increased with increasing methyl substitution up to four methyl. However, the molecular weights and polydispersities stayed of the polyethylene produced remained constant.

Polymerisations of ethylene using AMO-Mg_3Al-CO_3/MAO/(^{Mes}PDI)$FeCl_2$ in a 2 L steel reactor demonstrated a three fold increase in activity compared to 100 mL glass ampoule.

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Notes and references

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