

Metalloocene supported core@LDH catalysts for slurry phase ethylene polymerisation

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We report the synthesis of solid catalysts based on a zirconocene supported on either silica@AMO-LDH or zeolite@AMO-LDH for the slurry phase polymerisation of ethylene. The hybrid catalysts demonstrate synergistic effects in which the polymerisation activity is up to three times higher than the zirconocene supported on analogous single phase silica or zeolite supports.

The use of zeolites, silicas and layered double hydroxides (LDHs) as effective catalyst supports has been reported for a wide range of reactions.^{1,2} Amongst these, there is an ever-increasing demand to find viable and competitive catalyst supports of single-site catalysts for heterogeneous polyethylene synthesis. The central focus of this research field is now balancing product distribution, performance, cost and scalable solutions.³⁻⁶

A significant number of structural features effect the interaction between the support and active catalytic components, and hence the success of the support, these include the shape, size, size distribution and connectivity of the pores present in the material.⁷ It has been reported that as pore diameters of the support become increasingly narrow, catalytic activity is reduced.^{7,8} This is thought to be for two main reasons, firstly that the reduced proximity between the active species assists the formation of inactive bimolecular species,^{7,8} and secondly that reactant diffusion rates can be suppressed by the formation of surface blocking deposition.⁸ In this sense, the prospect of using mesoporous materials as catalyst supports is a promising area of investigation.⁹ Similarly, it has also been noted that acidic properties of such supports may prove beneficial. For example, Costa Vayá *et al.* have shown that the productivity in ethylene polymerisation using ZSM-5 supported catalysts correlates with an increase in surface acidity. This, along with surface Si:Al ratio have been found to be influential factors that affect the binding of

methylaluminoxane (MAO) onto the zeolite surface.¹⁰

It has been shown that silica, zeolites and LDHs are promising candidates for use as catalyst supports for polyethylene production.^{6,9-21}

Recently, we have reported that highly dispersed, organophilic LDHs (AMO-LDHs),²² prepared using the aqueous miscible organic solvent treatment (AMOST) method are highly effective supports for single-site ethylene polymerisation,¹⁹ and oligomerisation catalysis.²⁰ More recently, we have reported the synthesis of silica@AMO-LDH and zeolite@AMO-LDH hybrid core@shell materials.^{23,24} Herein, we now report the use of these materials for the immobilisation of a prototypical group 4 metallocene and their use as solid ethylene polymerisation catalysts.

The core@AMO-LDH hybrid materials, SiO₂@AMO-LDH, ZSM-5@AMO-LDH and HY@AMO-LDH {ZSM-5 (Si:Al = 23); HY (Si:Al = 5.1); AMO-LDH = Mg₃Al-CO₃ = [Mg_{0.75}Al_{0.25}(OH)₂](CO₃)_{0.18}•0.2H₂O•0.1acetone} were synthesised using the methods recently reported by us.^{23,24} Typical transmission electron microscopy images of these as synthesised hybrid support materials are shown in Fig. 1.

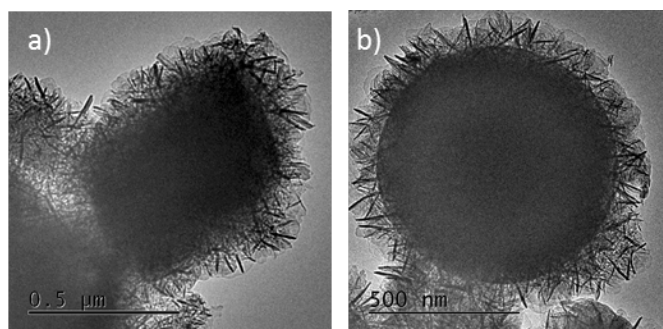


Fig. 1 TEM pictures of the core@LDH supports (a) ZSM-5@AMO-Mg₃Al-CO₃ and (b) SiO₂@AMO-Mg₃Al-CO₃ used during this study.

SiO₂@Mg₃Al-CO₃, ZSM-5@Mg₃Al-CO₃ and HY@Mg₃Al-CO₃ and hybrids require an methylaluminoxane (MAO) pre-treatment step before immobilisation of the metallocene-based single-site catalyst.²⁷ In this manuscript, MAO has been omitted from

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the catalysts formulae for clarity. This pre-treatment is necessary as metallocene-based polymerisation catalysts are known to irreversibly deactivate on inorganic supports that have a high concentration of surface hydroxyl groups. In this study we choose *rac*-ethylenebis(indenyl)zirconium dichloride (*rac*-(EBI)ZrCl₂) as the single-site metallocene pro-catalyst for immobilisation due to its extensive use in both academia and industry.^{26,28} The zirconium loading was calculated by using a 200:1 ratio of MAO:*rac*-(EBI)ZrCl₂ in all supports. Using this ratio all the *rac*-(EBI)ZrCl₂ binds to the solid support. All the polymerisation studies were conducted as a hexane slurry under 2 bar ethylene.²⁵ Triisobutylaluminium (TIBA) was added to the reaction mixture as a water and oxygen scavenger, prolonging the lifetime of the catalyst.²⁹

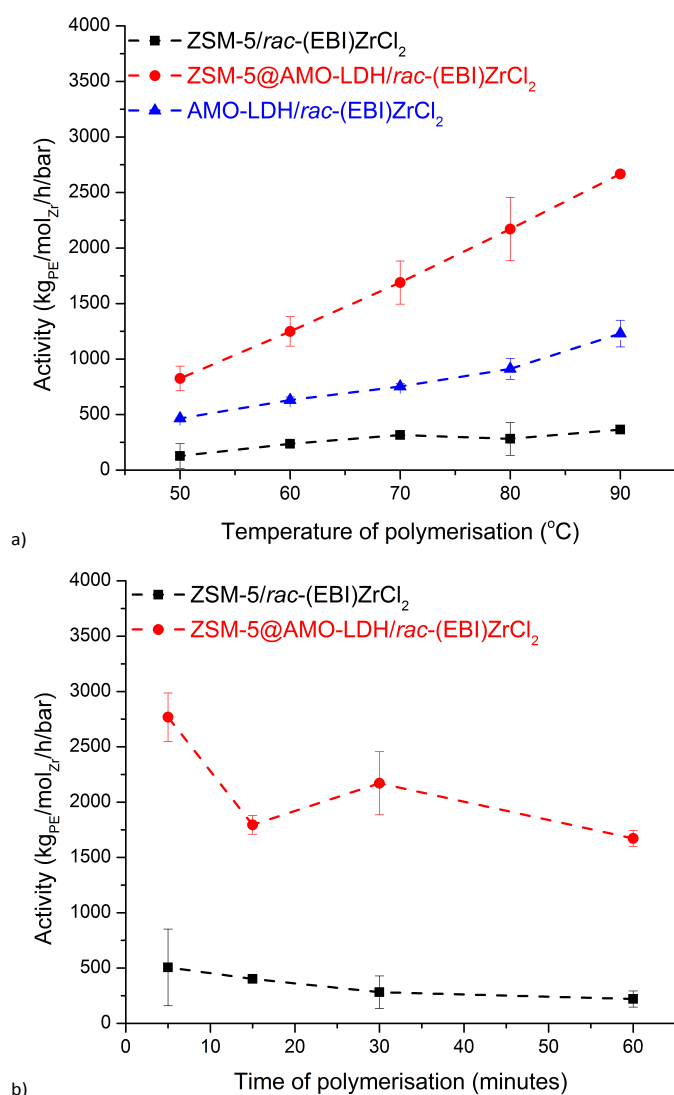


Fig. 2 Ethylene polymerisation activities versus a) temperature and b) time for ZSM-5/*rac*-(EBI)ZrCl₂ (black square), ZSM-5@AMO-LDH/*rac*-(EBI)ZrCl₂ (red circle) and AMO-LDH/*rac*-(EBI)ZrCl₂ (blue triangle). Polymerisation conditions: 2 bar ethylene, Hexane (50 mL), supported catalyst (10 mg), TIBA (150 mg).

The ethylene polymerisation activity profiles of *rac*-(EBI)ZrCl₂ immobilised on the MAO-modified ZSM-5@AMO-LDH as a function of time and temperature is shown in Fig. 2. For

comparison, the figure also includes the activity data for *rac*-(EBI)ZrCl₂ immobilised on MAO-modified ZSM-5 and MAO-modified AMO-Mg₃Al-CO₃ LDH at the same catalyst loadings and polymerisation conditions.

Fig. 2a, shows an increase in activity with increasing temperature across all catalysts (up to 2667 kg_{PE}/mol_{Zr}/h/bar for ZSM-5@AMO-LDH/*rac*-(EBI)ZrCl₂). This is consistent with the findings reported by Michelotti *et al.* which has shown that an increase in temperature increases polymer productivity whilst decreasing the molecular weight of the polymer for Cp₂ZrCl₂ (Cp = η -C₅H₅) supported on zeolite HY.¹²

When comparing supports, it is very evident that the polymerisation activities of *rac*-(EBI)ZrCl₂ on the ZSM-5@AMO-LDH hybrid are significantly higher than when the metallocene is immobilised of either one of the single phase supports (2667, 1229 and 364 kg_{PE}/mol_{Zr}/h/bar for ZSM-5@AMO-LDH/*rac*-(EBI)ZrCl₂, AMO-LDH/*rac*-(EBI)ZrCl₂ and ZSM-5/*rac*-(EBI)ZrCl₂ respectively). These results suggest a positive synergistic interaction of the active site formed from *rac*-(EBI)ZrCl₂ and the ZSM-5@AMO-LDH hybrid. Fig. 2b, shows that the maximum polymerisation activity is reached in the first 10 minutes of the reaction, this behaviour has been previously reported for supported catalysts.²⁰ After 10 minutes, a reduction in catalytic activity is observed as the growing polyethylene chains in the reaction medium progressively hinder the {ethylene}-{supported catalyst} interaction. Typically, polymerisation activities tend towards a constant value as the system approaches the monomer diffusion controlled limit.³¹

In contrast, the catalytic activities of both HY@AMO-LDH/*rac*-(EBI)ZrCl₂ and AMO-LDH/*rac*-(EBI)ZrCl₂ are similar across all the temperatures tested, Fig. S1. For the HY@AMO-LDH sample, TEM studies demonstrate the presence of a significant degree of LDH coverage on the surface of the HY crystallites. One explanation for their similar performance may be due to blocking on the HY-LDH interface and HY core by the excess LDH coating so that they cannot contribute to the material's function as a catalyst support. Furthermore, the activities observed for the pure HY system, HY/*rac*-(EBI)ZrCl₂ are significantly higher in comparison to the other supports, suggesting that the HY contribution to activity in the HY@AMO-LDH has been minimal, Fig. S1.

Slurry phase ethylene polymerisation was carried out between 50 - 90 °C for 1 h in hexane with *rac*-(EBI)ZrCl₂ supported on MAO modified SiO₂@LDH (SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂) and AMO-LDH/*rac*-(EBI)ZrCl₂. A comparison of their polymerisation activities is shown in Fig. 3.

The temperature dependence of the polymerisation activity of SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂ shows a bell-shaped activity curve, this behaviour is typical for immobilised *rac*-(EBI)ZrCl₂, we found the optimum polymerisation temperature to be ca. 80 °C (Fig. 3). This response can be explained by a playoff on the increase in the chain propagation rate with temperature, and an increasing chain termination rate after the optimum temperature. At 80 °C the activity is 2494 kg_{PE}/mol_{Zr}/h/bar. At this optimum temperature the activity is 2.5 times higher than

the activity of the AMO-LDH/*rac*-(EBI)ZrCl₂ (911 kg_{PE}/mol_{Zr}/h/bar).

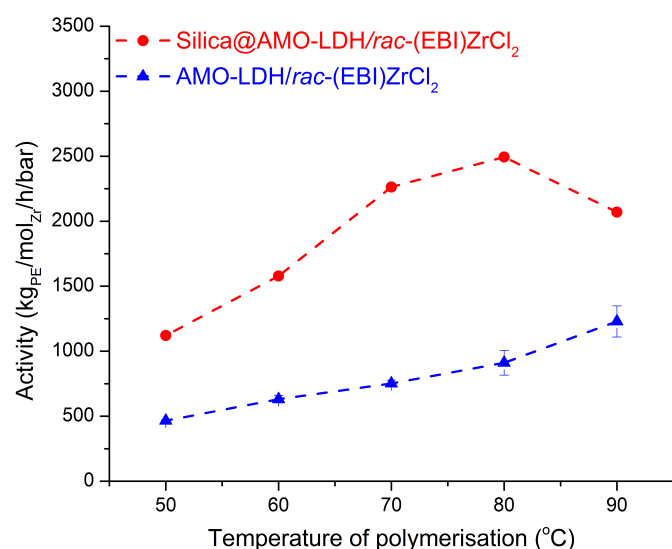


Fig. 3 Ethylene polymerisation activities versus temperature. (a) AMO-LDH/*rac*-(EBI)ZrCl₂ (blue triangle) and (b) SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂ (red square). Hexane (50 mL), Ethylene (2 bar), 1 h, TIBA : Catalyst 1000 : 1.

The temporal profile of the ethylene polymerisation activity for *rac*-(EBI)ZrCl₂ immobilised on both SiO₂@AMO-LDH and AMO-LDH have been determined (Fig. S2). Both AMO-LDH/*rac*-(EBI)ZrCl₂ and SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂ show an initial increase in polymerisation activity reaching a maximum activity, after 15 minutes, of 899 and 2406 kg_{PE}/mol_{Zr}/h/bar respectively.

Fig. 4 shows the SEM images of polyethylene produced using SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂.

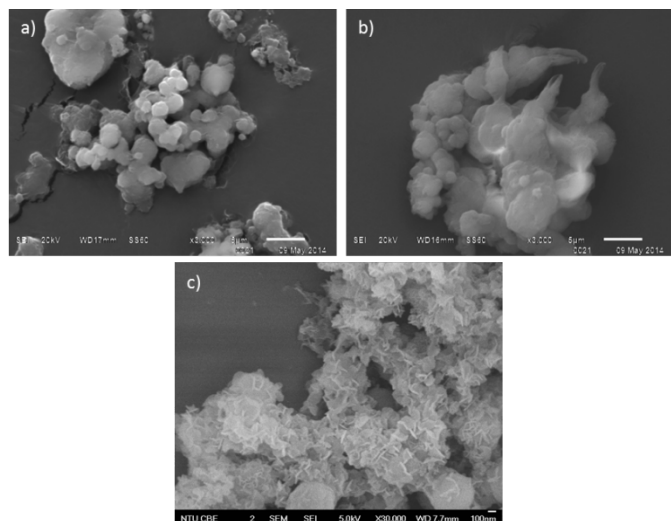


Fig. 4 SEM images of polyethylene obtained using SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂ after (a) 15 minutes, (b) 60 minutes and (c) image of SiO₂@AMO-LDH.

Fig 4a shows an image of the polyethylene particles produced after 15 minutes. Spherical polymer particles in the size range 1.3 - 1.9 μm and 6.3 - 10.3 μm are observed in the sample. The morphology of the polyethylene particles has mirrored the

catalyst support morphology to a certain extent; the original silica@AMO-LDH is shown in Fig 4c.²³ There are some particles that are ~760 nm; potentially the presence of the silica@AMO-LDH catalyst support particles. Fig 4b is an image of the sample after 1 h, the individual polymer particles have grown and aggregated together forming a very large polymer particle of 27 μm.

The molecular weight and polydispersities of the polyethylene formed using SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂ and AMO-LDH/*rac*-(EBI)ZrCl₂ are shown in Fig. 5. As expected, the molecular weights decreased with increasing temperature for both catalysts (from over 200,000 to under 100,000 kg/mol). The polydispersities are high for both catalysts (between 4 and 5), which similar to reported literature for AMO-LDH/*rac*-(EBI)ZrCl₂ based catalyst systems.¹⁹

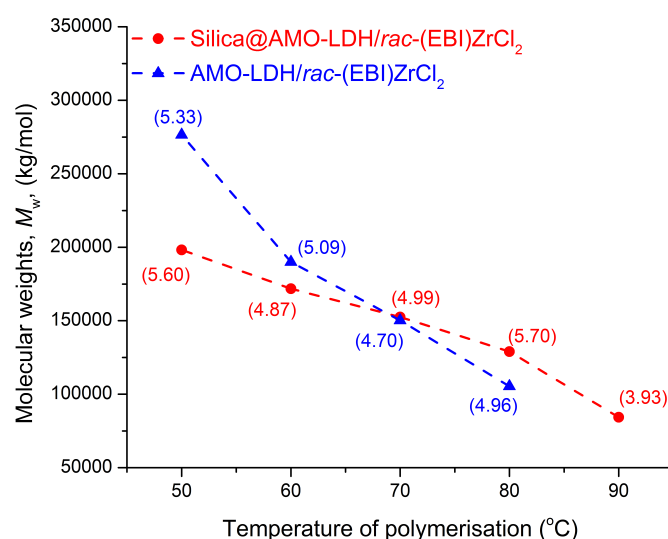


Fig. 5 Molecular weight and polydispersities, in parentheses, of the polyethylene synthesised using SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂ (red circle) and AMO-LDH/*rac*-(EBI)ZrCl₂ (blue triangle). Polymerisation conditions: Ethylene (2 bar), Hexane (50 mL), 1 h, TIBA (150 mg).

Conclusions

We have found that the hybrid core@AMO-LDH materials, SiO₂@AMO-LDH, ZSM-5@AMO-LDH and HY@AMO-LDH can be surface-modified with MAO and then used to immobilise the zirconocene complex *rac*-(EBI)ZrCl₂. These novel hybrid metallocene-support systems are highly active for slurry phase ethylene polymerisation. We observe higher polymerisation activities for ZSM-5@AMO-LDH/*rac*-(EBI)ZrCl₂ and SiO₂@AMO-LDH/*rac*-(EBI)ZrCl₂ compared to the analogous systems using single phase modified supported. Therefore, in these systems we seem to observe a synergistic contribution to catalytic activity as a result of the hybrid core@shell structure.

In contrast, the behaviour of HY@AMO-LDH/*rac*-(EBI)ZrCl₂ mimics that of AMO-LDH/*rac*-(EBI)ZrCl₂. Overall the results indicate that in a core@AMO-LDH system there is an optimum LDH coverage, which controls the accessibility, stability and /or activity of the the active site catalyst centre to the inorganic core, and inorganic core-LDH interface. The SEM images show

that the morphology of the polyethylene produced by the SiO₂@AMO-LDH supported metallocene complex is more desirable when compared to the polymer produced by the AMO-LDH supported metallocene complex, generating less aggregated and more spherical polymer particles.

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