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Metallocene supported core@LDH catalysts for slurry phase ethylene polymerisation

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1. General Details

General experimental details. All organometallic manipulations were performed under an atmosphere of N_2 using standard Schlenk line techniques or an MBraun UNIlab glovebox, unless stated otherwise. Hexanes and toluene were dried using an MBraun SPS 800 solvent purification system, degassed prior to use and stored over a potassium mirror. *rac*-(EBI)$ZrCl_2$ was obtained from Strem and used as received. Methylaluminoxane (MAO) was purchased from Sigma-Aldrich as toluene solution which was dried off to afford a free flowing colourless solid, and TIBA was obtained neat from Sigma Aldrich and used as received.

Thermal treatment of zeolite, silica, AMO-LDH, zeolite@AMO-LDH and silica@AMO-LDH. Samples of zeolite HY (Si:Al = 5.1) were thermally treated for at 150 °C for 6 h under vacuum (10^{-2} mbar) to ensure removal of surface and co-intercalated water. This process was also repeated for samples of HY@AMO-LDH, ZSM-5 (Si:Al = 23), ZSM-5@AMO-LDH, Silica and AMO-LDH.

Support pre-treatment with MAO. Two equivalents of each thermally treated sample (750 mg) were heated with one equivalent of methylaluminoxane (MAO) (363 mg) in 50 mL toluene at 80 °C for 2 h. A molecular weight of 60 amu was assumed for all supports for ease of calculation. The solvent was then filtered and dried under vacuum for 4 h to form the relevant catalyst precursor. This process was repeated for all of the thermally treated samples outlined in Section 5.4.2. Yields as stated in square brackets: HY/MAO [93%], ZSM-5/MAO [77%], ZSM-5@AMO-LDH/MAO [78%], silica@AMO-LDH/MAO [89%] and AMO-LDH/MAO [50%]. In the manuscript, these MAO modified supports are shortened to HY, ZSM-5, ZSM-5@AMO-LDH, silica@AMO-LDH and AMO-LDH respectively

Preparation of supported catalyst. One equivalent (500 mg) of support pre-treated with MAO and 0.005 equivalents (5.88 mg) of *rac*-(EBI)$ZrCl_2$ was heated in toluene (40 mL) at 60 °C for 1 h initially using an oil bath, and then 80 °C for a second hour where appropriate if the solution was not clear and colourless. This was then filtered and dried under vacuum for 4 h to obtain the relevant supported catalyst. Yields as stated in square brackets: HY/MAO/*rac*-(EBI)$ZrCl_2$ [90%], HY@AMO-LDH/MAO/*rac*-(EBI)$ZrCl_2$ [86%], ZSM-5/MAO/*rac*-(EBI)$ZrCl_2$ [85%], ZSM-5@AMO-LDH/MAO/*rac*-(EBI)$ZrCl_2$ [83%], silica@AMO-LDH/MAO/*rac*-(EBI)$ZrCl_2$ [89%] and AMO-LDH/MAO/*rac*-(EBI)$ZrCl_2$ [86%]. In the manuscript, these MAO modified catalysts

are shortened to HY@AMO-LDH/*rac*-(EBI)$ZrCl_2$, ZSM-5/*rac*-(EBI)$ZrCl_2$, ZSM-5@AMO-LDH/*rac*-(EBI)$ZrCl_2$, silica@AMO-LDH/*rac*-(EBI)$ZrCl_2$ and AMO-LDH/*rac*-(EBI)$ZrCl_2$.

Ethylene polymerisation studies. The prepared catalysts were investigated for their ability to act as catalysts for the polymerisation of ethylene under slurry conditions in the presence of TIBA (150 mg). The reactions were performed with ethylene (2 bar) in a 200 mL ampoule, with a noted value of ca. 10 mg of supported catalyst as prepared above, suspended in hexane (50 mL). Following reaction, the polyethylene product was isolated by filtration using a sintered glass frit with washing in 50 mL pentane. These reactions were carried out at 50, 60, 70, 80 and 90 °C for all prepared catalysts, and at 5, 15, 30 and 60 minutes.

2. Polymerisation reactions

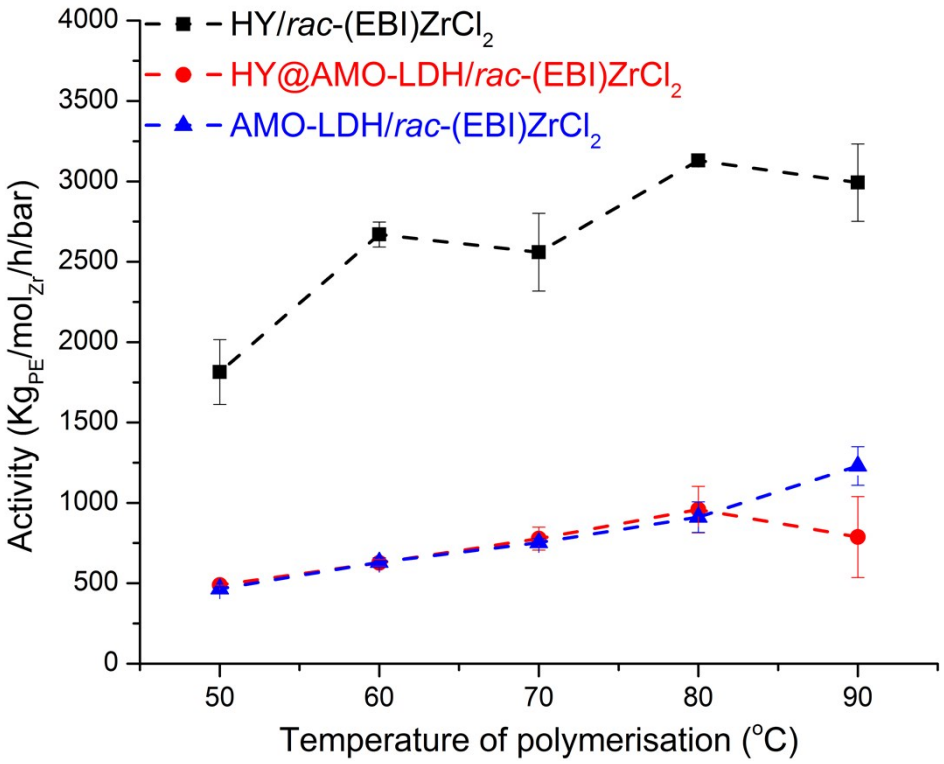

Fig. S1 Polymerisation activities of HY/*rac*-(EBI)$ZrCl_2$ (black square), HY@AMO-LDH/*rac*-(EBI)$ZrCl_2$ (red circle) and AMO-LDH/*rac*-(EBI)$ZrCl_2$ (blue triangle). Polymerisation conditions: Ethylene (2 bar), 30 minutes, Hexane (50 mL), Supported catalyst (10 mg), TIBA (150 mg).

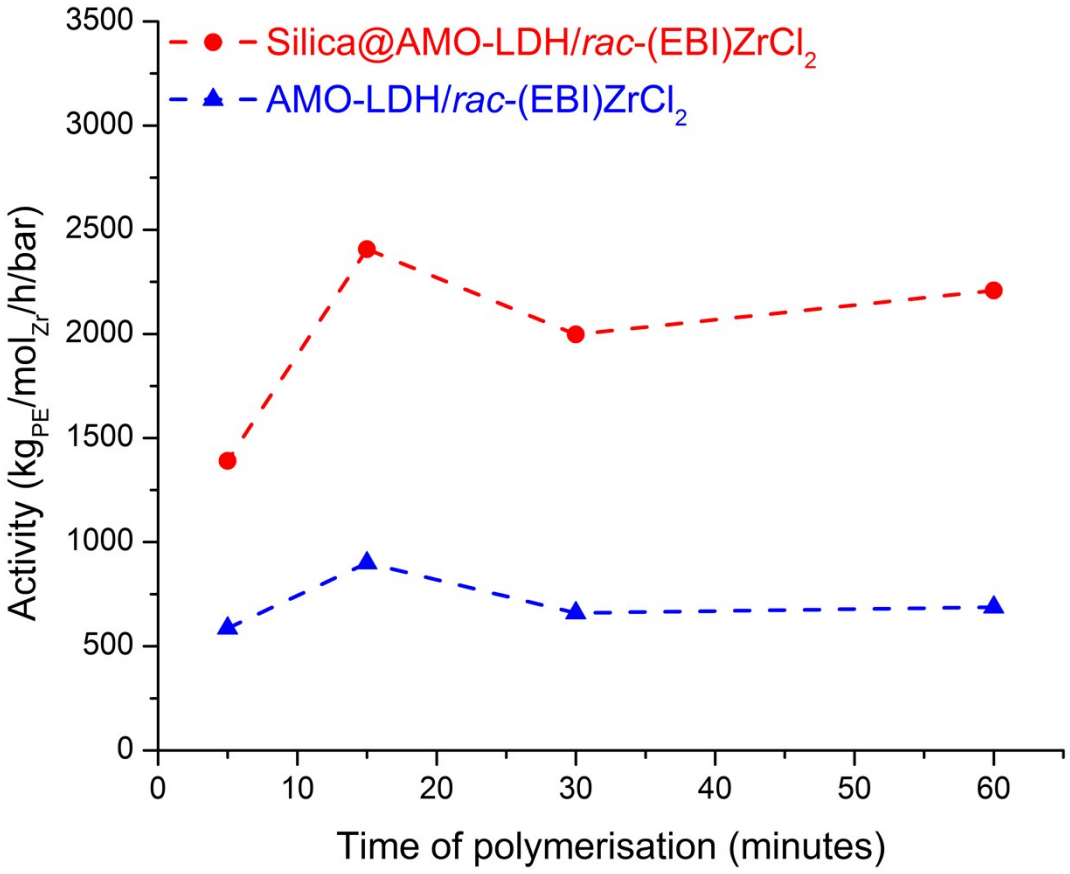

Fig. S2 Polymerisation activities versus time of polymerisation for silica@AMO-LDH/*rac*-(EBI)$ZrCl_2$ (red circle) and AMO-LDH/*rac*-(EBI)$ZrCl_2$ (bleu triangle) Polymerisation conditions: Ethylene (2 bar), 80 °C, Hexane (50 mL), Supported catalyst (10 mg), TIBA (150 mg).

3. Scanning electron microscopy

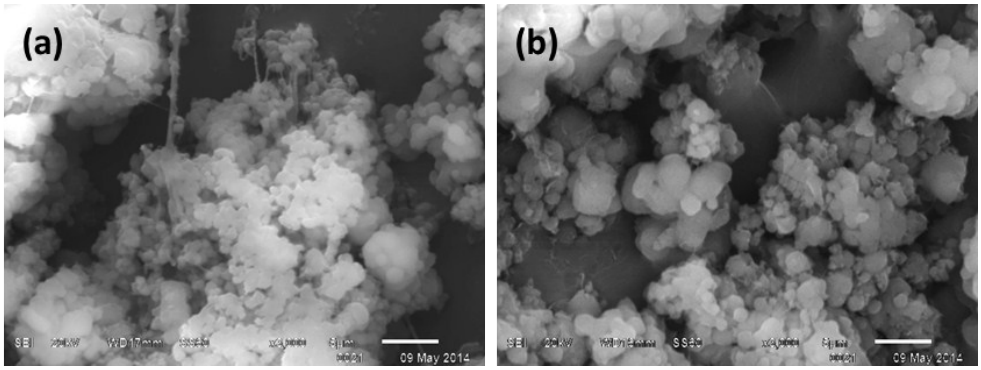

Fig. S3 SEM images of polymer produced using the AMO-LDH/*rac*-(EBI)$ZrCl_2$ catalyst support complex after (a) 15 minutes and (b) 60 minutes.