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The design of a bipodal bis(pentafluorophenoxy)aluminate supported on silica as an activator for ethylene polymerization using surface organometallic chemistry

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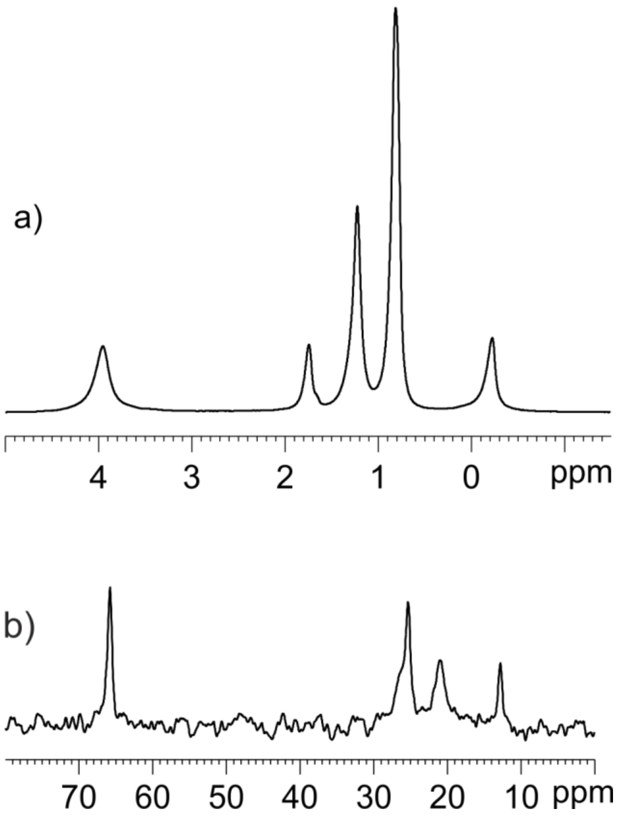

Figure S1. Solid -State NMR spectra of $[(\equiv SiO)_2Al(iBu)(Et_2O)]$ (a) ^{1}H MAS (800 MHz, 16 scans, relaxation delay of 2 s, 20 kHz spinning speed); and (b) ^{13}C CPMAS (125.5 MHz, 8 k scans, relaxation delay of 2 s, 10 kHz spinning speed)

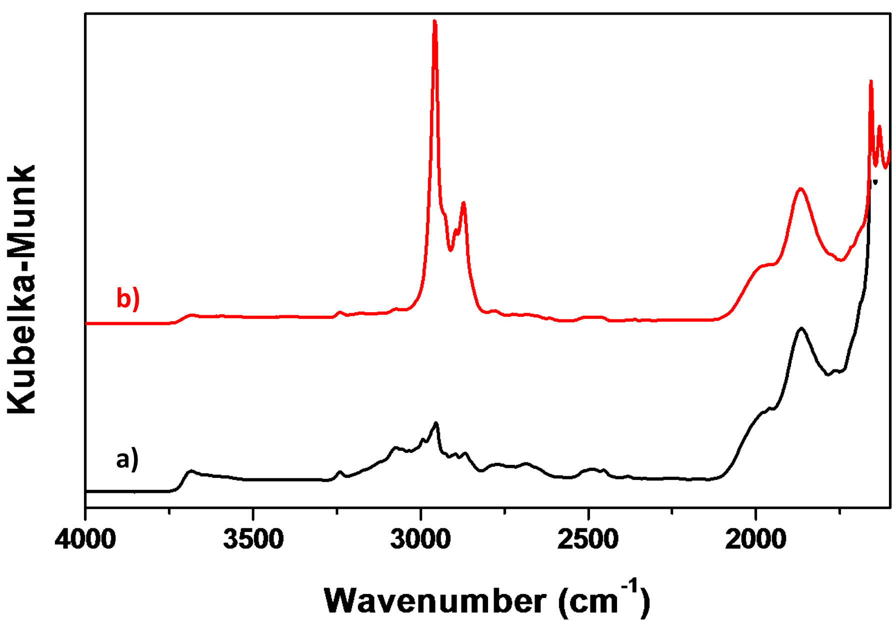

Figure S2. DRIFT spectra of **AS-1** (a) and after reaction with Al(*i*Bu)$_3$ (b)

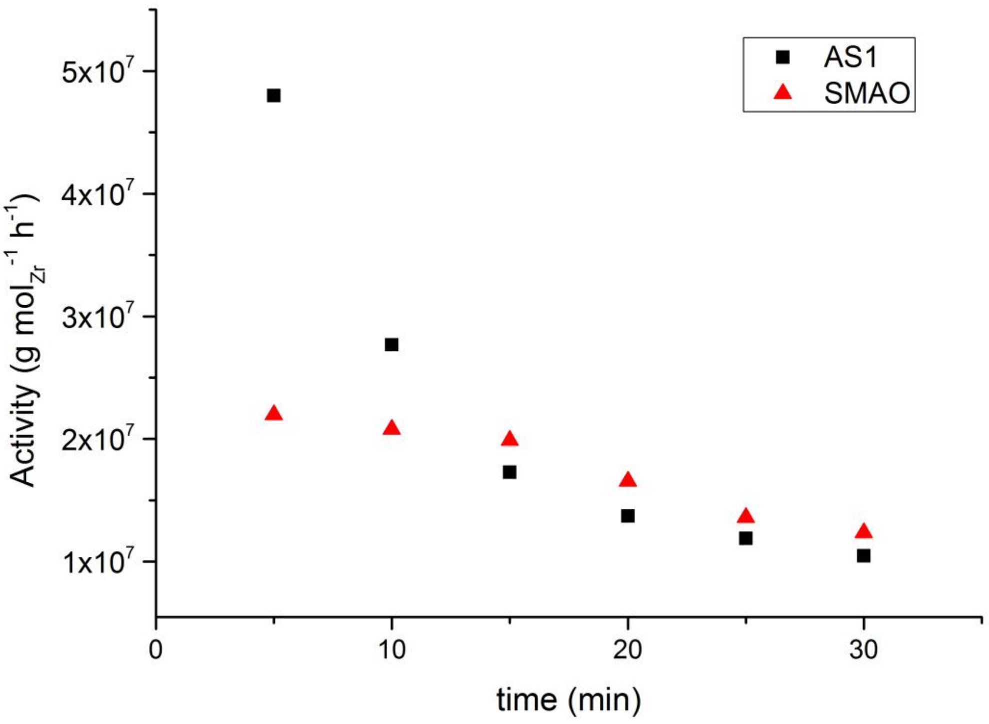

Figure S3. Kinetic profiles for ethylene/1-hexene copolymerization using *rac*-$EtInd_2ZrCl_2$ in association with the activating support **AS-1** and SMAO

Table S1. Physical properties of the polymers obtained with the different catalysts

Catalyst	mol% hexene	T_{fusion} (°C)	Crystallinity (%)	$X_{1\text{-hexene}}$[a] mol%	Mn[b] (g mol^{-1})	Đ[b]
AS1/ *rac*-EtInd$_2$ZrCl$_2$	-	133	61	-	41 700	3.1
	19.5	118	39	1.5	46 600	4.2
AS1 / (*n*BuCp)$_2$ZrCl$_2$	-	135	76	-	72 800	2.1
	19.5	124	48	0.6	53 900	2.5
SMAO$_{600}$/ *rac*-EtInd$_2$ZrCl$_2$	-	135	61	-	36 100	3.3
	19.5	119	45	1.8	37 000	5.4
SMAO$_{600}$/ (*n*BuCp)$_2$ZrCl$_2$	-	133	65	-	36 100	2.2
	19.5	123	56	0.7	34 800	2.2

a) Determined by ^{13}C NMR. [b] Determined by high temperature SEC using a polyethylene calibration.

Experimental Section

General

All experiments were performed under a controlled atmosphere by using Schlenk and glove-box techniques for organometallic syntheses. For the synthesis and treatments of the surface species, reactions were performed by using high-vacuum lines (1 mPa) and glove boxes. Diethyl ether, heptane and benzene were distilled on NaK–benzophenone and degassed through freeze–pump–thaw cycles. 1-hexene was distilled over CaH_2 prior to use. Ethylene (purity 99.95%) was purchased from Air Liquide. The gas was passed through three different purification columns before use: a first one filled with reduced BASF R3-16 catalyst (CuO on alumina), a second one filled with molecular sieves (13X, 3A, Sigma–Aldrich) and a final one filled with Selexsorb COS (Alcoa). Elemental analyses were performed at the Mikroanalytisches Labor Pascher, Remagen (Germany). Gas-phase analyses were performed on a Hewlett–Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an Al_2O_3/KCl on fused silica column (50 m x 0.32 mm). DRIFT spectra were recorded on a Nicolet 6700 FTIR spectrometer by using airtight cells. NMR spectra in solution were recorded on DRX300 Bruker instruments. Solid-state ^{13}C CPMAS NMR spectra were recorded on a Bruker Avance500 spectrometer with a conventional double-resonance 4 mm CPMAS probe and on a Bruker Avance800 spectrometer with a conventional double-resonance 3.2 mm MAS probe. Solid-state ^{1}H and ^{27}Al MAS NMR spectra were recorded on a Bruker Avance III 800 spectrometer with a conventional double-resonance 3.2 mm MAS probe. Chemical shifts were given with respect to TMS as the external reference for ^{1}H and ^{13}C NMR spectroscopy, to $CFCl_3$ for ^{19}F NMR spectroscopy and to $Al(H_2O)_6^{3+}$ for ^{27}Al.

For the characterization of polymers, high-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for the ^{1}H nucleus, and 101 MHz for ^{13}C. Spectra were recorded at 393 K using a 5 mm QNP probe for ^{1}H NMR, and a PSEX 10 mm probe for ^{13}C. Polymer samples were examined as 5-15 % (w/v) solutions. A mixture of trichlorobenzene (TCB) and deuterated toluene (C_7D_8) (2/1 v/v) was used as solvent. Chemical shift values are given in units of ppm, relative to an internal reference of tetramethylsilane for ^{1}H NMR and to the methylenes of PE at 30 ppm for the ^{13}C NMR. Thermal characterizations were performed with a differential scanning calorimetry, Mettler Toledo DSC 1, equipped with an auto-sampler and a 120 thermocouple sensor. The temperature and the heat flow of the equipment were calibrated with an indium standard. All samples were accurately weighed (between 5 to 10 mg) and sealed in aluminum pans. They were heated from -20 °C to 180 °C at 10 °C min^{-1} with an empty aluminum pan as reference. Two successive heating and cooling were performed and only the second run was considered. Dry nitrogen with a flow rate set at 50 mL min^{-1} was used as the purge gas. The melting temperature (Tm) was measured at the top of the endothermic peak. The STARe thermal analysis software is used to calculate the melting temperature and the crystallinity of the copolymers: $X = \Delta Hf / \Delta Hf0$ where ΔHf (J g^{-1}) is the melting heat of the sample and $\Delta Hf0$ (= 293 J g^{-1}) the melting heat of a 100 % crystalline polyethylene. High temperature Size Exclusion Chromatography (HT-SEC) analyses were performed using a Viscotek system (from Malvern Instruments) equipped with three columns (PPS POLEFIN 1 000 000Å, 100 000Å and 1 000Å). 200 µL of sample solutions with concentration of 5 mg mL^{-1} were eluted in 1,2,4-trichlorobenzene using a flow rate of 1 mL min^{-1} at 150°C. The mobile phase was stabilized with 2,6-di(tert-butyl)-4-methylphenol (200 mg L^{-1}). The OmniSEC software was used for data acquisition and data analysis. The molecular weight distribution were calculated with a calibration curve based on narrow poly(ethylene) standards (M_p : 338, 507, 750, 1180, 2030, 22000, 73000, 99000, 126000 g mol^{-1}) from Polymer Standard Service (Mainz). SEM images have been observed on a FEI Quanta 250 FEG microscope, after metallization of the samples by a carbone plait evaporation on a Balzers MED010 apparatus.

Synthesis of activating support (AS1). Silica Aerosil from Evonik with a specific area of 200 m² $g.^{-1}$ was calcined at 500 °C for 4 h, then dehydroxylated at 700 °C for 12 h under high vacuum (1 mPa). $[(\equiv SiO)_2Al(i\mathrm{Bu})(Et_2O)]$ was prepared according to literature procedures (mass balanced analysis: Al, 0.8 wt%; C, 3.9 wt%).[1] 1.0 g (0.27 mmol) of the grafted isobutylaluminum $[(\equiv SiO)_2Al(i\mathrm{Bu})(Et_2O)]$ was reacted for 30 min with 0.15 mL of a 2 M solution of diethylaniline (in toluene, 0.3 mmol, 1.1 *eq.*), and then with 125 mg (0.68 mmol 2.5 *eq.*) of pentafluorophenol in benzene overnight at room temperature in a double-Schlenk flask. After filtration the solid was washed three times with benzene. After evaporation of benzene, the solid was washed once again with pentane. The resulting white powder (1.63 g) was dried under vacuum and stored in a glove box. Elemental analysis: Al, 0.7 wt%; N, 0.4 wt%; C, 6.5 wt%.

Synthesis of SMAO catalyst ($SMAO_{600}$). The silica impregnated with MAO, named hereafter as SMAO, was prepared as follows. 2 g of silica Grace 948 dehydroxylated at 600 °C were placed in a three neck round bottom flask in the glove box under Argon. An amount of dry toluene equal to the pore volume of silica i.e., 1.7 ml g^{-1} was mixed with 3.5 ml of 30 wt% MAO solution in a separate vial at room temperature under argon and left for 30 min. This solution of MAO in toluene was then added to the silica drop-wise which wetted the silica completely. Then this thick slurry was heated at 80°C for 4h without any stirring under argon and the evaporating toluene was refluxed with the help of a condenser. At the end of this process, the mixture once washed with 5 ml of heptane and then dried under vacuum at 80 °C. Dried SMAO, a free flowing white powder, was stored in glove box.

Supported metallocene catalysts were synthesized by adding 2 g of SMAO in the three neck round bottom flask and adding a 10 mL solution of (nBuCp)$_2$ZrCl$_2$ or *rac*-Et(Ind)$_2$ZrCl$_2$ (by aiming Al/Zr molar ratio of 150 in the final catalyst) in toluene drop-wise at room temperature under argon. The volume of toluene solution was just enough to wet the silica completely by filling its pores. The slurry was then heated for 1 h at 50 °C followed by one heptane wash (5 ml) and vacuum drying at 50 °C for few hours. Finally a free flowing catalyst was obtained which was then stored in a glove box. Elemental analysis: (*rac*-EtInd$_2$ZrCl$_2$/SMAO): Zr, 0.34 wt%; Al, 12.1 wt% (n-BuCp)$_2$ZrCl$_2$/SMAO): Zr, 0.26 wt%; Al, 11.4 wt%.

Polymerization procedure. Polymerizations were performed in a 500 mL glass reactor equipped with a stainless steel blade stirrer and an external water jacket for temperature control. The activating support, the needed quantity of the *rac*-Et(Ind)$_2$ZrCl$_2$ or (n-BuCp)$_2$ZrCl$_2$ (from a 2 mM solution in toluene) and Al(iBu)$_3$ (at a concentration of 1.0 mM solution in heptane) were pre-contacted in a small round bottom flask in 10 mL of heptane. Meanwhile the required quantity of Al(iBu)$_3$ and 1-hexene were introduced in a flask containing 300 mL of heptane. The catalyst mixture was transferred in the flask. This mixture was then immediately introduced in the reactor under a stream of argon. The argon was then pumped out before introducing the ethylene. Temperature and pressure were then progressively increased up to 80 °C and 4 bar. The pressure was kept constant during the polymerization. After 30 min of reaction, the polymerization was stopped. The resulting mixture was poured in 400 mL of methanol. The polymer was collected by filtration, washed with methanol, and dried under vacuum.

Remark: When SMAO/metallocene catalysts were used, the required quantity of solid catalyst and scavenger (Al(iBu)$_3$) were associated together in 10 mL of heptane and the subsequent procedure remained unchanged.

Reference

1 J. Pelletier, J. Espinas, N. Vu, S. Norsic, A. Baudouin, L. Delevoye, J. Trébosc, E. L. Roux, C. Santini, J.-M. Basset, R. M. Gauvin and M. Taoufik, *Chem. Commun.*, 2011, **47**, 2979–2981.