Supporting Information

A strategy For High Ethylene Polymerization Performance Using Titanium Single-Site Catalysts

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- **General procedure**

All experiments were carried out under a controlled atmosphere. Treatments of the surface species were carried out using high vacuum lines (1.34 Pa.) and glove box techniques. Pentane was distilled on Na-benzophenone and degassed through freeze pump thaw cycles. Hydrogen was dried over freshly regenerated molecular sieves (3 Å) and deoxy traps.

- **Catalysts preparation:**
  - **Preparation the support**

KCC-1 was obtained from KAUST Catalysis Center, other supports were synthesized according to the literature.

  - **Synthesis of SBA-15**

To obtain the SBA-15, 8 g of the amphiphilic triblock copolymer poly (ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) or PEG-PPG-PEG (P123) was dissolved in 250 mL acidic solution with 1.9 N (in a graduate test tube 211 mL of distillate water and 39 mL of acid chloride 37 wt.%). Immersing the flask in an oil bath at 40 °C and stirring it at 500 rpm. After three hours 17 g of tetraethyl orthosilicate (TEOS) was added drop by drop. Maintain the mixture at 40 °C and stir for 24 h. The mixture then was placed in an autoclave and heated at 100 °C in the oven for 24 h. After that, a Buncher filtration with 1 L of distillate water was performed and left at room temperature of 24 h. The white powder was collected in a tube and calcined with a ramp of 60 °C/h for 16 h at 550 °C.

  - **Support Preparation Process**

Generation of the isolated silanol groups required treatment at high temperature under vacuum (10^{-5} mbar), 2 g of KCC-1 or SBA-15 was introduced to a quartz reactor fitting a tubular furnace, and the treatment starting with dehydration by heating up to 130 °C for 3 h, followed by dihydroxylation at 700 °C, for 16 to 20 hours, a heating gradient is 1 °C/min. After thermal treatment, titration with Methyl Lithium was performed, using ether as a solvent, Quantification of the released Methane indicate that the amount of silanol groups [≡Si-OH] is 1.8 mmol.g^{-1} of KCC-1 and 1.7 mmol.g^{-1} of SBA-15$_{700}$

The reaction of the silanol surface group of KCC-1(or SBA-15), dehydroxylated at 700 °C (1.8 mmol.g^{-1} of [≡Si-OH] obtained by titration of MeLi) with DIBAL (1 eq. per [≡Si-OH]) occurs at room temperature in dry and degassed pentane for 1 h (Scheme S1), and DIBAL/Si-OH was found to be 1.1. During the reaction, 1.2 isobutyls per grafted Al is released and quantified by GC analyses.

The results are similar to those obtained during the reaction of DIBAL with SBA-15 and, neither H_2 nor isobutene was detected in the gas phase. [(≡Si-O-Si≡) (≡Si-O)$_2$-Al-H] was generated through a thermal treatment (400 °C for 24 h, rate 18 °C/h) under a high vacuum (10^{-5} bar) of [(≡Si-O-Si≡) (≡Si-O)$_2$-Al-^{i}Bu].
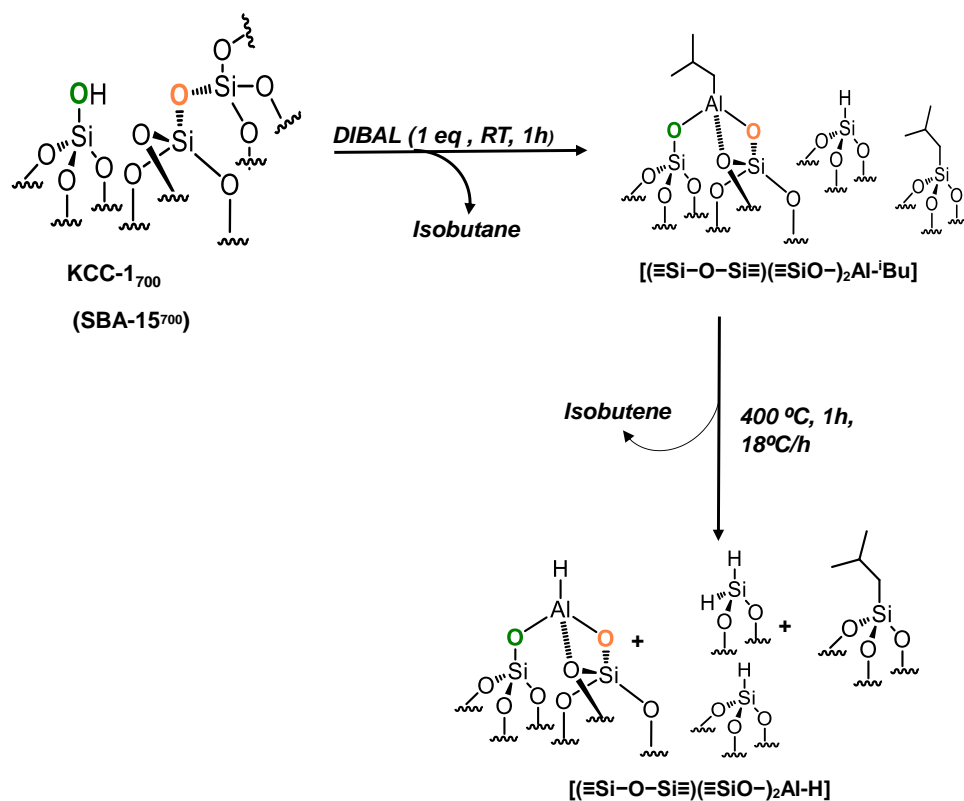
Scheme S1. Preparation of Al-H support.[1]

The oxidation step of [Al-H] was successfully achieved through the reaction of 0.7 bar of N_2O at 100 °C, for two days.
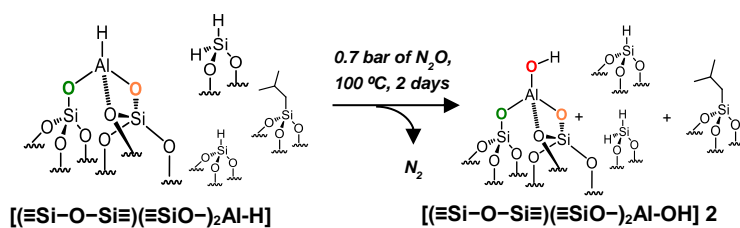

Scheme S2. Oxidation of [(≡Si−O−Si≡)(≡SiO−)$_2$Al-H] to generate [(≡Si−O−Si≡)(≡SiO−)$_2$Al-OH] **2.**
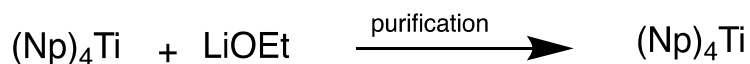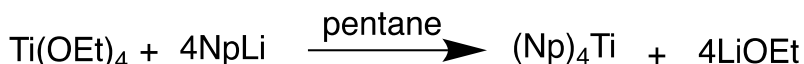
- **Preparation of Titanium neopentyl**

All preparation procedures were carried out under an inert atmosphere. Solvents were collected from a solvent purification system and degassed through freeze-pump-thaw cycles. The metallic precursors were prepared according to the literature procedure. 3 g of Lithium weirs were heated

at 180 °C for 30 min, and 50-60 mL of dry hexane was added to the lithium wires, followed by drop-by-drop addition of 12 mL of chloride neopentyl. The mixture was heated at 75 °C in the oil path and under the distillation system for 8 days.

$$NpCl \quad + \quad Li \quad \xrightarrow{\text{hexane}} \quad NpLi \quad + \quad LiCl$$
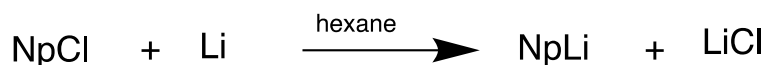
Neopentyl lithium was filtered and dried to remove all of the solvents. Next, in the glovebox fill a glass reactor with 4 eq. of lithium neopentyl, 50-60 mL of dried and degasses pentane were added since the reaction was carried out at -80°C using a mixture of acetone and dry ice, and then 1 eq. of titanium-tetra ethoxide was added drop by drop. The reaction was allowed to reach room temperature slowly and remained at that temperature for 24 h. The reaction mixture was filtered and dried under a dynamic vacuum. The crude product was purified by vacuum sublimation to obtain a pure yellow solid of Ti (Np)$_4$. In the glovebox, 1 mg of the Titanium neopentyl was introduced in a low-pressure Liquid NMR tube along with 1 mL of deuterated solvent (C_6D_6), and liquid ^{1}H-NMR and ^{13}C-NMR was performed (results detailed bellow).

$$Ti(OEt)_4 + 4NpLi \quad \xrightarrow{\text{pentane}} \quad (Np)_4Ti \quad + \quad 4LiOEt$$

$$(Np)_4Ti \quad + \quad LiOEt \quad \xrightarrow{\text{purification}} \quad (Np)_4Ti$$

- **Preparation of the grafted catalysts (1, 3, 4 and 5)**

The grafting process was carried out using stander double-Schlenk, 0.5 eq. (with respect to the amount of accessible silanol) of Titanium tetra-neopentyl, and excess pentane are put to one part of the double-Schlenk, where KCC-1$_{-700}$ or SBA-15 is added to the other part. The solution is transferred to the KCC-1$_{-700}$ (or SBA-15) through the filter.

After 4 h, the reaction was stopped, and the liquid phase was filtered into the other part of the double-Schlenk by inversing its position. Three washing, and filtration cycles are performed, and the remaining solvent is removed by the high vacuum line technique. The solid product is collected and stored in a storage tube in the glovebox.

- **Catalysts Characterizations:**

 a. **Liquid State Nuclear Magnetic Resonance Spectroscopy**

The spectra were recorded on Bruker Avance 400 MHz spectrometers. The chemical shifts were measured comparatively to ^{1}H or ^{13}C resonance in the deuterated solvents C_6D_6 (7.16 ppm for ^{1}H and 128.06 ppm for ^{13}C).

In the glovebox, 1 mg of the Titanium neopentyl was introduced in a low-pressure Liquid NMR tube along with 1 mL of deuterated solvent (C_6D_6)

^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.24 [s, 8H, CH$_2$], δ 1.18 [s, 36H, CMe$_3$]. ^{13}C NMR (400 MHz, C$_6$D$_6$) δ 119.6 [CH$_2$], δ 37.6 [CMe$_3$], δ 34.5 [CMe$_3$]. The ^{1}H and ^{13}C NMR data is consistent with the literature data.[2]
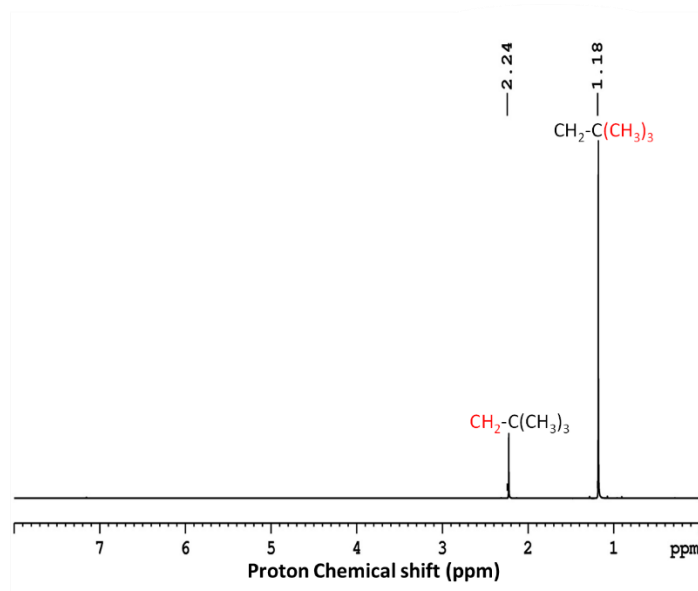
Fig. S1. ^{1}H-Liquid state NMR spectrum of TiNp$_4$.
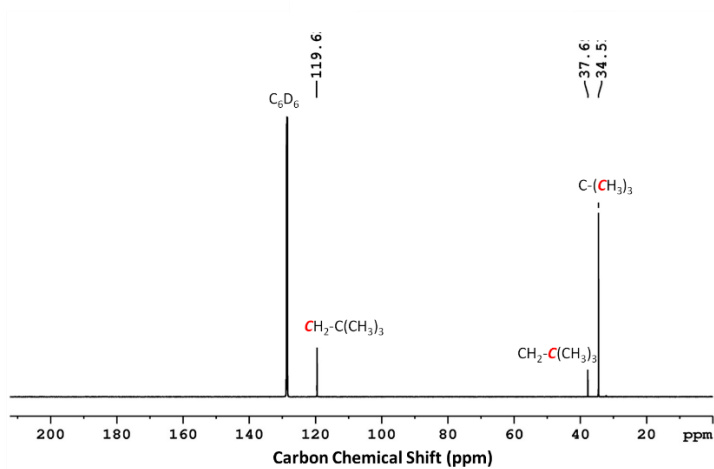
Fig. S2. ^{13}C Liquid state NMR spectrum of TiNp$_4$.

b. Nitrogen adsorption/desorption measurements

Nitrogen adsorption/desorption measurements Typical isotherms of all materials are shown in the table below. It is a classical type IV isotherm, which bears a characteristic H1 hysteresis loop. A type IV isotherm indicates monolayer adsorption followed by multilayer formation and capillary condensation.

Table S1. Nitrogen adsorption/ desorption values of the supports

| Sample	BET surface area $(m^2.g^{-1})$	pore volume $(cm^3.g^{-1})$	pore diameter (nm)
KCC-1	725	1.24	7.57
SBA-15	776	0.95	6.1

c. FT-IR spectroscopy

Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a cell under a controlled atmosphere. For FT-IR analysis, The IR samples were prepared under argon within a glovebox. Typically, 25 mg of each sample was pressed at high pressure onto a pellet.
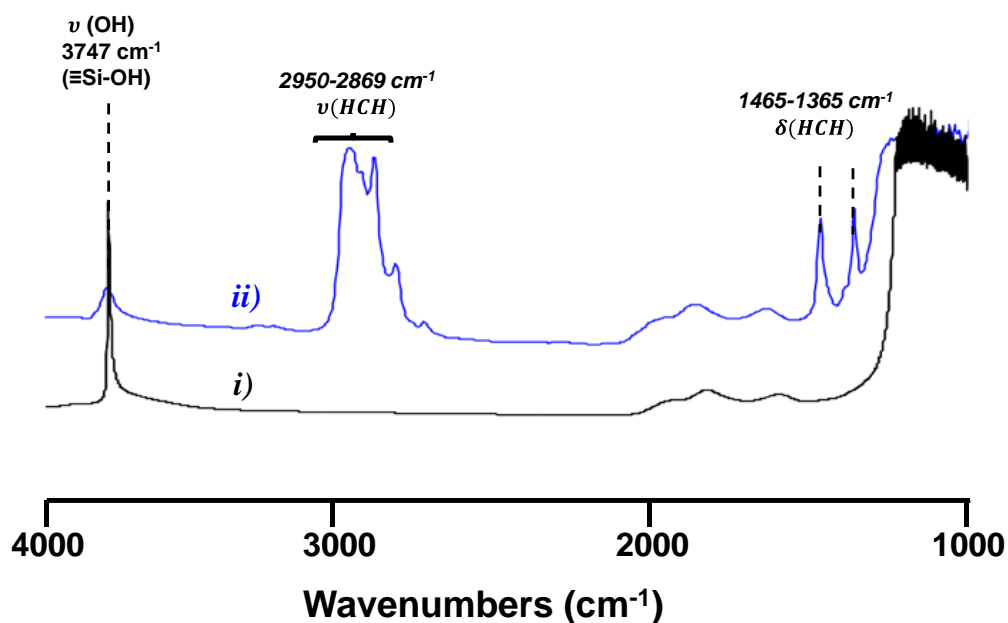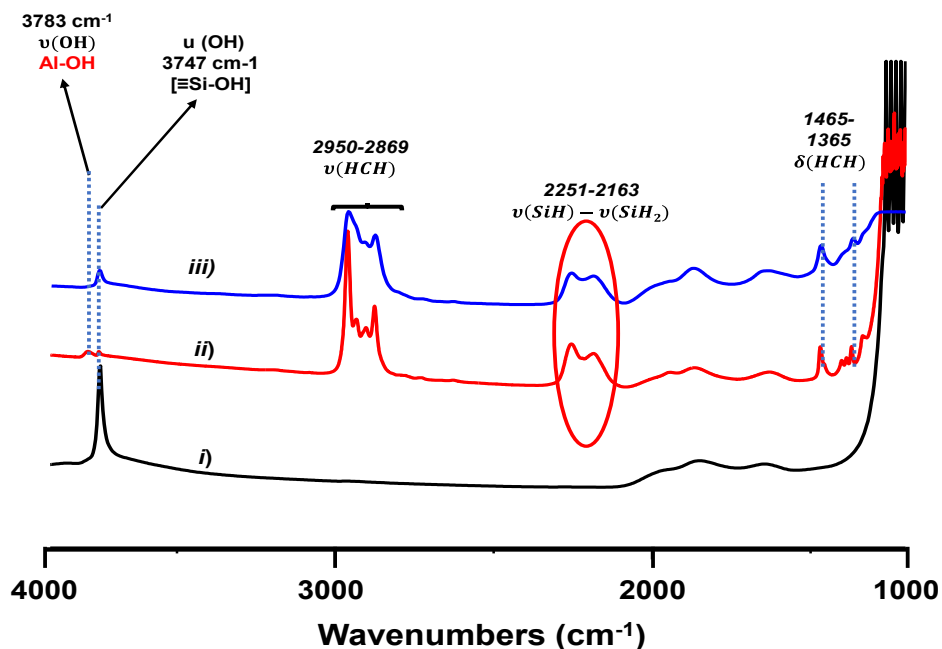

Fig.S3. FT-IR spectra of *i)* KCC-1$_{700}$ and *ii)* KCC-1$_{700}$ [(≡Si−O−)TiNp$_3$], **1**.
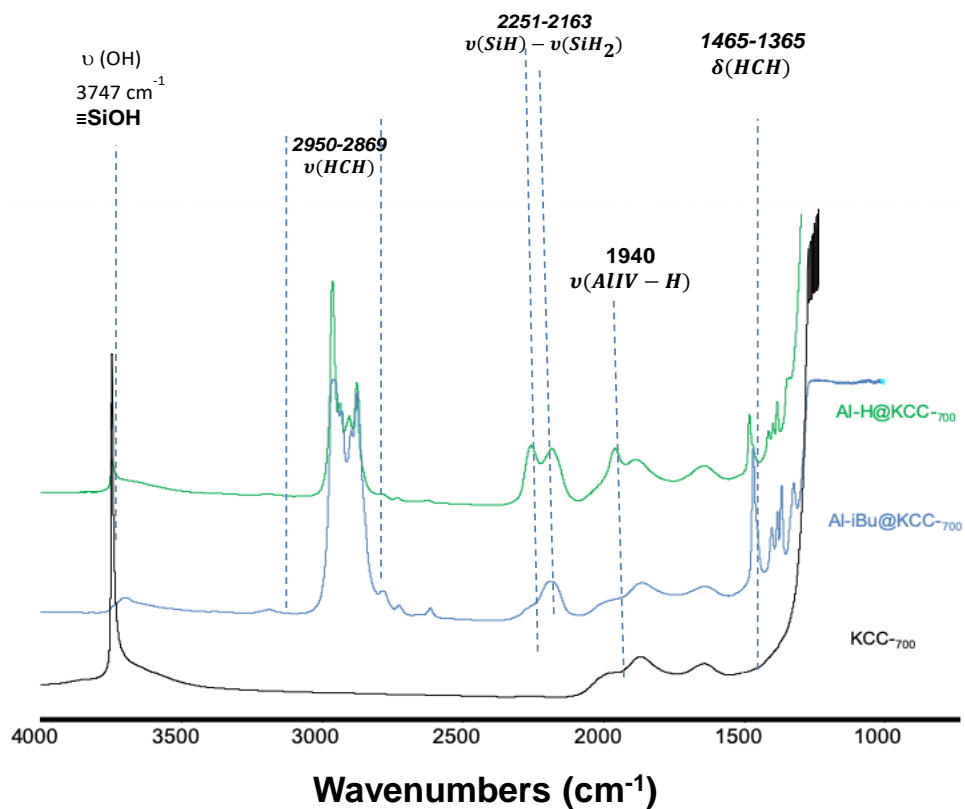
Fig. S4. FT-IR spectra of *i)* KCC-1$_{700}$ (black curve), *ii)* [(≡Si−O−Si≡)(≡SiO−)$_2$Al-^{i}Bu] (blue curve) *iii)* [(≡Si−O−Si≡)(≡SiO−)$_2$Al-H] (green curve).
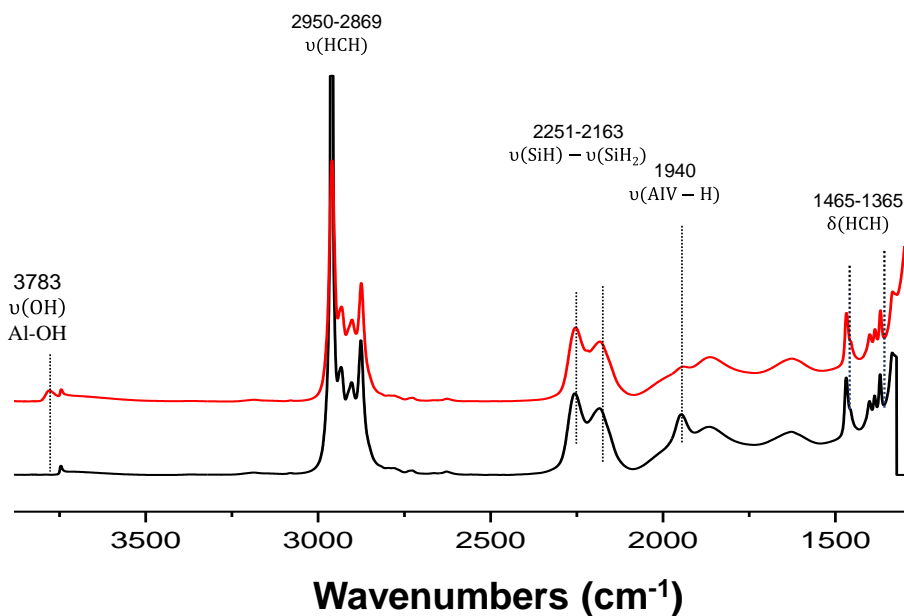
Fig. S5. FT-IR spectra of [(≡Si−O−Si≡)(≡SiO−)$_2$Al-H] (black curve), [(≡Si−O−Si≡)(≡SiO−)$_2$Al-OH] (red curve) **2**.

Fig. S6. The FT-IR spectrum of *i)* **SBA-15$_{700}$** (black curve), *ii)* [(≡Si−O−Si≡)(≡SiO−)$_2$Al-OH] (red curve) *iii)* [(≡Si−O−)$_2$(Al−O−)$_2$TiNp$_2$] (blue curve).
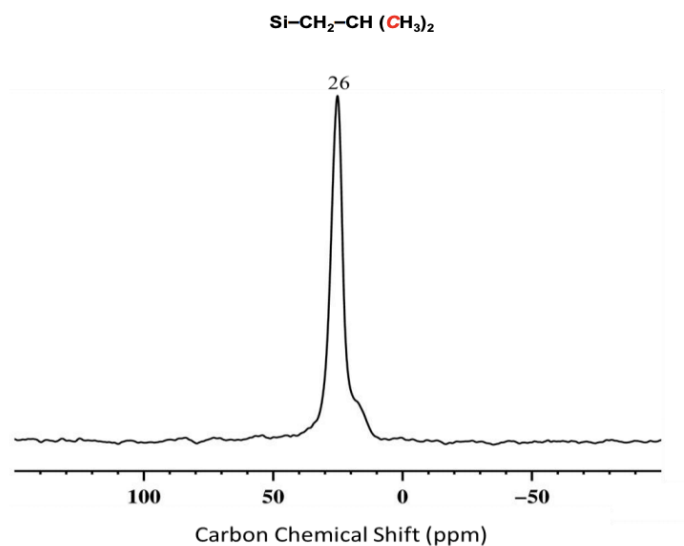
d. Solid-State Nuclear Magnetic Resonance Spectroscopy

^{13}C CP/MAS solid-state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 or 600 MHz resonance frequencies, with a conventional double resonance 4 mm CP/MAS probe at 400 MHz and 3.2 mm HCN triple resonance probe at 600 MHz.
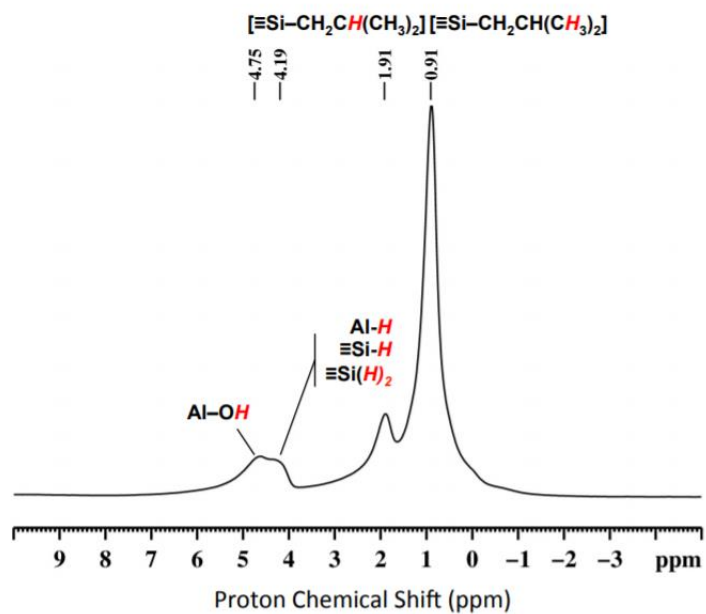
The ^{27}Al NMR spectra were obtained from Bruker AVANCE III spectrometer operating at 900 MHz for 1H with a conventional double resonance 3.2 mm CP/MAS probe with a recycling time of 1 s and a short pulse time of 1 µs.

Each sample was introduced into a rotor under an argon atmosphere and tightly closed. NMR chemical shifts are reported with respect to the external references, TMS, and adamantane.
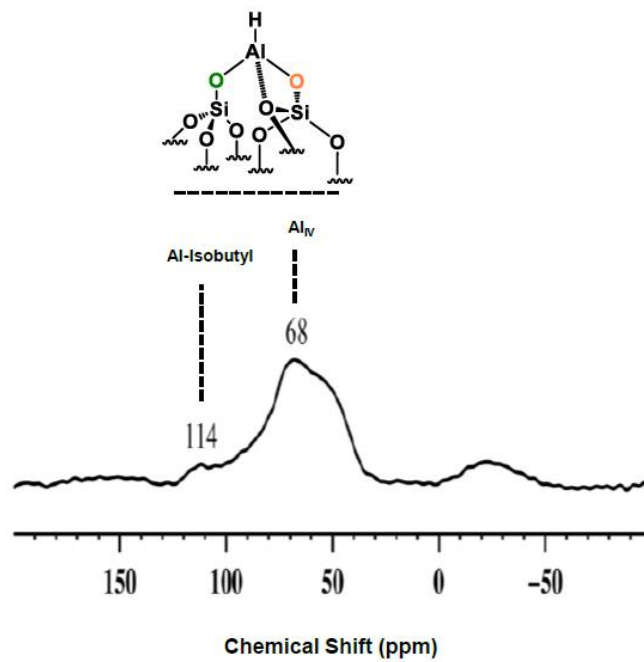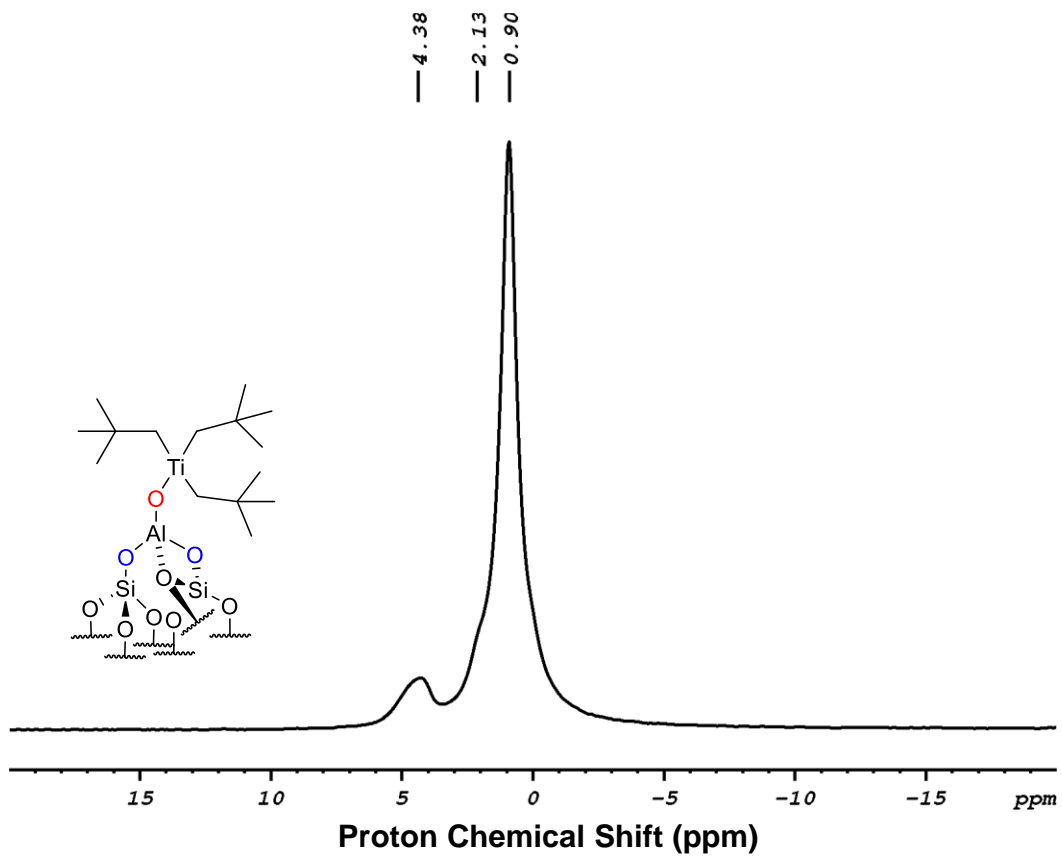
Si−CH₂−CH (*C*H₃)₂

Fig. S7. ^{13}C MAS-NMR spectra of [(≡Si−O−Si≡)(≡SiO−)₂Al-OH] **2**.

[≡Si−CH₂C*H*(CH₃)₂] [≡Si−CH₂CH(C*H*₃)₂]

−4.75
−4.19
−1.91
−0.91

Al-*H*
≡Si-*H*
≡Si(*H*)₂

Al−O*H*

Fig. S8. One dimensional ^{1}H NMR of [(≡Si−O−Si≡)(≡SiO−)₂Al-OH] **2** [3].

Fig. S9. ^{27}Al solid-sate NMR of the of [(≡Si−O−Si≡)(≡SiO−)$_2$Al-H] [1].

Fig. S10. The ^{1}H-MAS NMR spectrum of [(≡Si−O−)$_2$Al−O−Ti−Np$_3$]**, complex 3.**
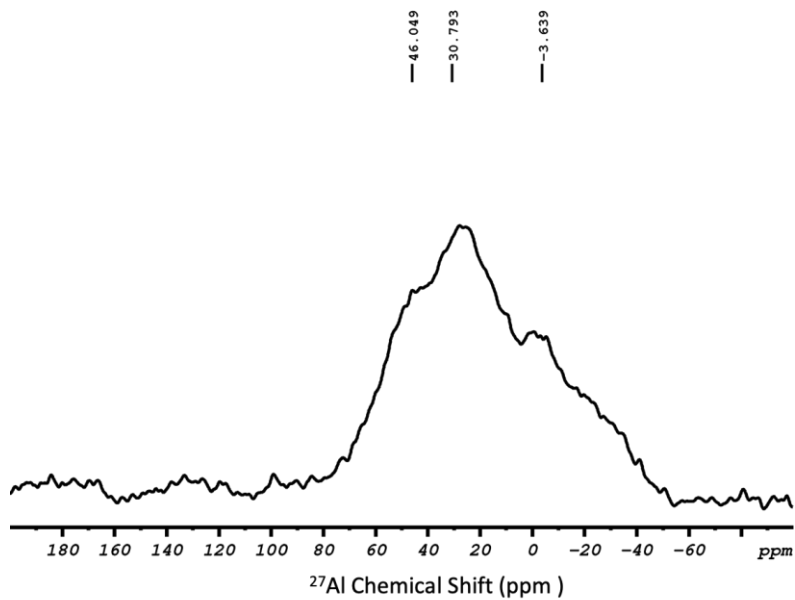
Fig. S11. ^{27}Al solid-state NMR of [(≡Si−O−)$_2$Al−O−Ti−Np$_3$], **complex (3).**

e. XPS analysis

X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hv = 1486.6 eV) operating at 45 W, a multichannel plate and delay line detector under a vacuum of 10^{-9} mbar. The high-resolution spectra were collected at fixed analyzer pass energies of 20 eV. Samples were mounted in a floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the sp3 hybridized (C-C) carbon for the C 1s peak set at 284.8 eV. XPS investigations were performed to characterize the chemical composition of the surface of the powdered samples. The samples were mounted on the holder in a glovebox under argon and then transferred to the XPS instrument using a transfer vessel for air-sensitive samples.
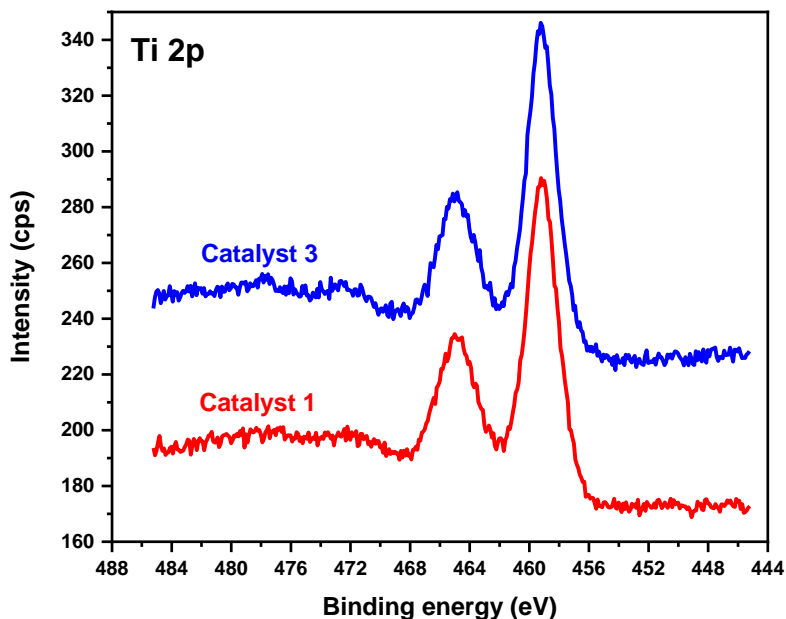

Fig. S12. High-resolution XPS spectra of Ti 2p region for catalysts **1** and **3**.
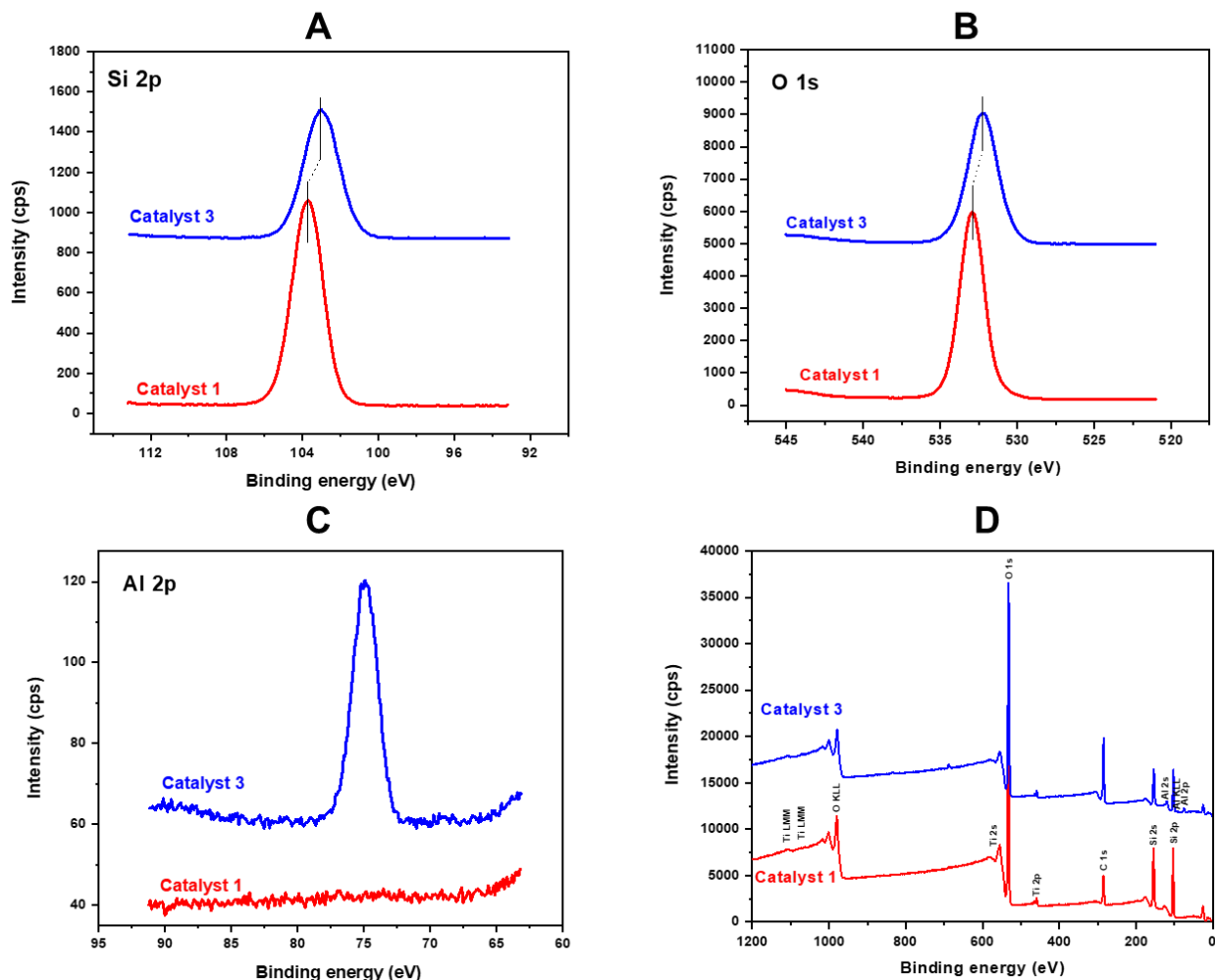
Fig. S13. High-resolution XPS spectra: **A)** Si 2p region; **B)** O 1s region; **C)** Al 2p region for catalysts **1** and **3**. **D)** Survey spectra for catalysts **1** and **3**.

f. TEM analysis

The morphology of **3** was examined by transmission electron microscopy (TEM). This task was accomplished by using a double aberration-corrected (double Cs corrected) microscope of model Titan 80-300 ThemisZ from Thermo-Fisher Scientific (Waltham, MA). Samples were loaded onto holey-carbon-coated copper grids for TEM analysis. The samples were placed onto grids in a solvent-free but ambient environment. The conventional bright-field TEM (BF-TEM) imaging technique was performed by operating the scope at the accelerating voltage of 300 kV.
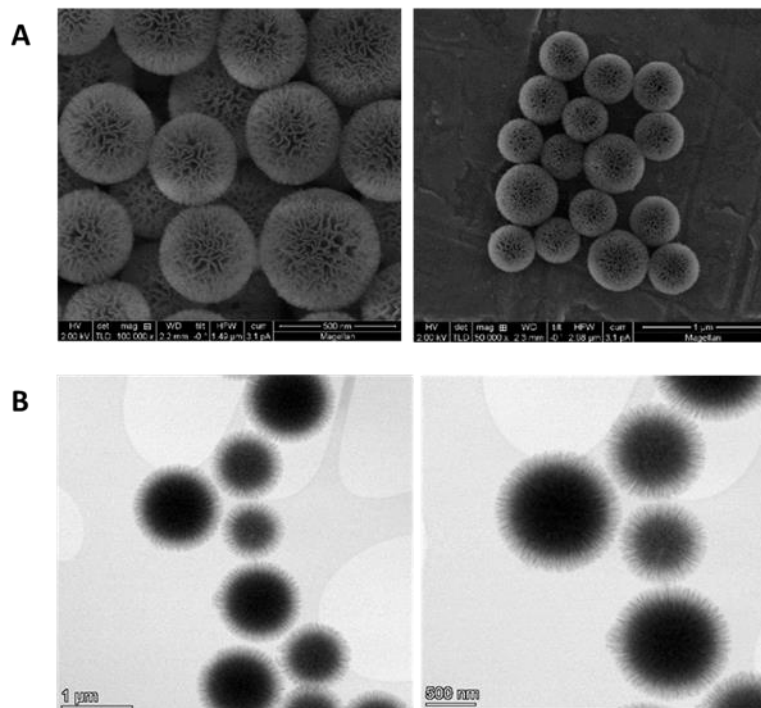
Fig. S14. A) SEM analysis for the KCC-1 after dehydroxylation at 700 °C. B) Low-magnification BF-TEM analysis of catalyst **3.**

g. Elemental Analysis

The analytical technique Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is used to determine the metal loading percentage in each complex while the CHN analyzer determines the carbon fractions.

For KCC-1$_{700}$

Since the Al-modified support contains carbon (3.2 mmol.g^{-1}), the total amount of carbon after grafting was 6.9 wt.% (5.7 mmol.g^{-1}); this value involves the amount of carbon remaining on the support as [≡Si–^{i}Bu]. To find the C/Ti ratio, which corresponds to the neopentyl ligands, we subscribe the total amount of carbon by the amount of carbon present on the support to determine the amount of carbon resulting from grafting the organometallic complex

$C_{\text{(carbon of [3])}} = C_{\text{(total carbon])}} - C_{\text{(carbon from ≡Si-isobutyl on modified support)}}$

$= 5.7 - 3.2 = 2.5 \text{ mmol.g}^{-1}$

For SBA-15$_{700}$

The Al-modified support contains carbon (6.3 wt.%, 5.2 mmol.g^{-1}), and the total amount of carbon after grafting was (8.7 wt.%, 7.3 mmol.g^{-1})
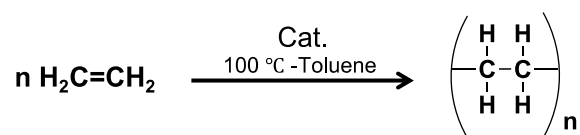
So:

$C_{(carbon\ of\ [5])} = C_{(total\ carbon|)} - C_{(carbon\ from\ \equiv Si\text{-}isobutyl\ on\ modified\ support)}$

$$= 7.3 - 5.2 = 2.1\ mmol.g^{-1}$$

Table S2. Elemental analysis of the various supported catalysts prepared with KCC-1$_{700}$ or SBA-15$_{700}$.

Catalysts	Al wt.%	Ti wt.%	Al mmol.g^{-1}	Ti mmol.g^{-1}	Al/Ti	C wt.%	C mmol.g^{-1}	C/Ti (Theo. Value)
1	NA	2.18	0.00	0.45	-	8.6	7.2	16 (15)
3	3.1	0.92	1.14	0.19	6		2.5	13.2 (15)
4	NA	1.82	0.00	0.38	-	4.4	3.7	9.7 (10)
5	5.2	0.97	1.8	0.2	9.5	2.1	1.7	8.5 (10)

- **Catalytic Test: Ethylene polymerization**

1- **Experimental procedure.** In a glovebox, an autoclave of 80 mL was charged with 50 mg of catalysts and 7 mL of dry and degassed toluene as solvent. The reactor was then heated to 100 °C, and purged under argon for 5 min. A 20 bar ethylene pressure was established and kept constant over the 1 hour of the reaction time. After 1 h under stirring, the resulting solid was filtered off and washed with water (80 mL), then was solubilized in 1,2, 4 Trichlorobenzene (TCB) at 200 °C. The solution was precipitated drop by drop in the methanol at room temperature to recover the initial structure of polyethylene (PE). The polyethylene (PE) obtained was dried out under a vacuum at room temperature.

$$n \ H_2C{=}CH_2 \xrightarrow[100\ °C\ \text{-Toluene}]{\text{Cat.}} \left(\begin{array}{c} H \ \ H \\ | \ \ \ | \\ C{-}C \\ | \ \ \ | \\ H \ \ H \end{array}\right)_n$$

Scheme S3. Ethylene polymerization

2- **Polymers characterization**

a. **High-Temperature Gel permeation chromatography**

Molecular weights and molecular weight distributions of the resulting polymers were determined by high-temperature gel permeation chromatography (HT-GPC) at 150 °C using 1,2,4-trichlorobenzene (TCB) as the solvent and using narrow molecular weight distribution polystyrene for calibration.

The resulting polymer was filtered off from the solvent and washed with water (80 mL), then was solubilized in 1,2,4-trichlorobenzene at 150 °C. The solution was precipitated drop by drop in the methanol at room temperature to recover the initial structure of polyethylene. The obtained polyethylene was dried under a vacuum at room temperature.

b. **Differential scanning calorimetry**

DSC (scanning calorimetry) analysis was carried out using Mettler TOLEDO DSC-1 equipment with the Stare software. In the standard DSC run mode under a nitrogen atmosphere. The polymer sample (2-3 mg), was heated from 25 to 180 °C at a rate of 10 °C/min to remove thermal history, before cooling to 25 °C at 10.8 °C/min. A second heating cycle at 10 °C/min was used for the determination of the peak melting temperature, Tm_2.
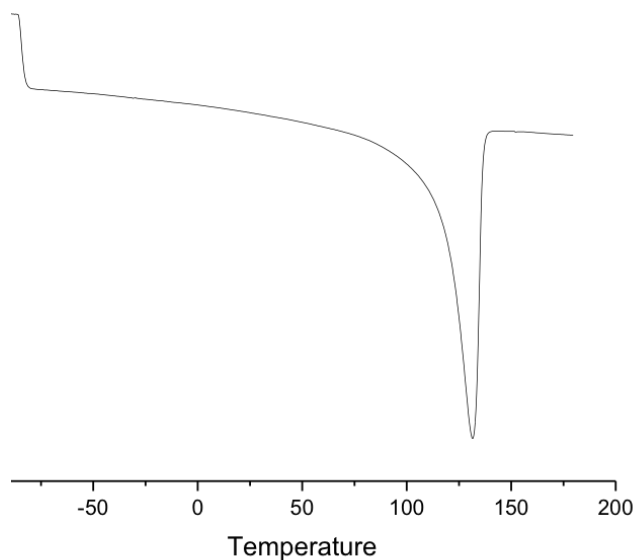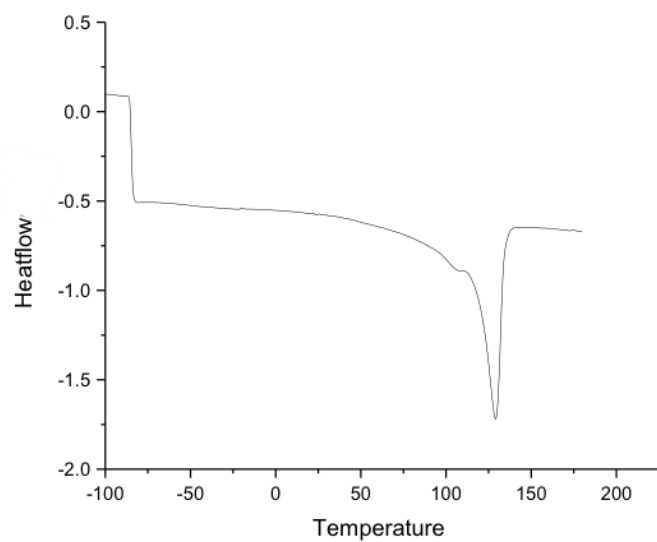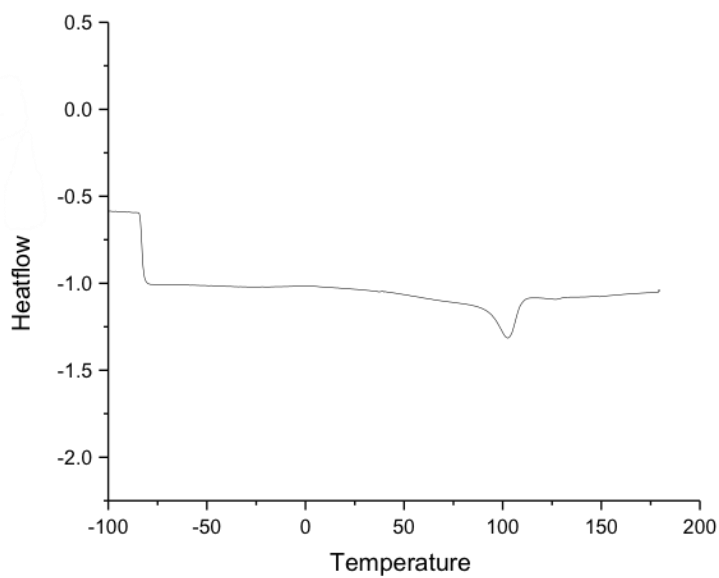
Fig. S15. DSC curve of a heating run of HDPE in the temperature range 25-180 °C, **(P3)** resulting from catalyst KCC-1 [(≡Si−O−)$_2$AlO−Ti−(CH$_2$CMe$_3$)] **3**, with a melting degree of 131 °C
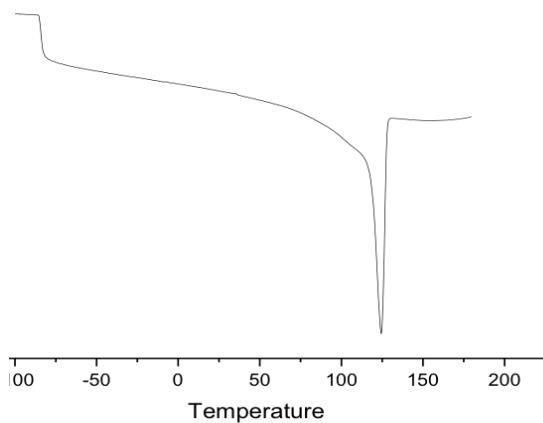
Fig. S16. DSC curve of a heating run of HDPE in the temperature range 25-180 °C, for **(P1)** resulting from catalyst KCC-1 [(≡Si−O−Ti−(CH$_2$CMe$_3$)$_3$] **1,** a melting point of 124 °C.

Fig. S17. DSC curve of **(P5)** resulting from catalyst SBA-15 [((≡Si−O−)₂Al-O)₂−Ti−(CH₂CMe₃)₂] **5**, heating run of HDPE in the temperature range 25-180 °C, the melting point of 129 °C

Fig. S18. DSC curve of **(P4)** resulting from catalyst SBA-15 [(≡Si-O-)₂Ti-(CH₂CMe₃)₂] heating run of LDPE in the temperature range 25-180 °C. The melting point of 102 °C
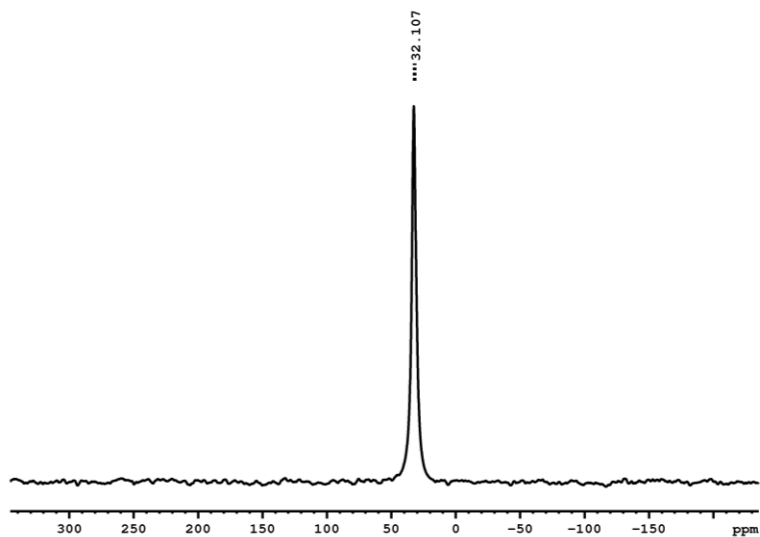
The ^{13}C MAS-NMR spectrum of polymers shows a major single at 32 ppm attributed to the carbon backbone (-CH$_2$-C-) indicating that both polymers are liner.
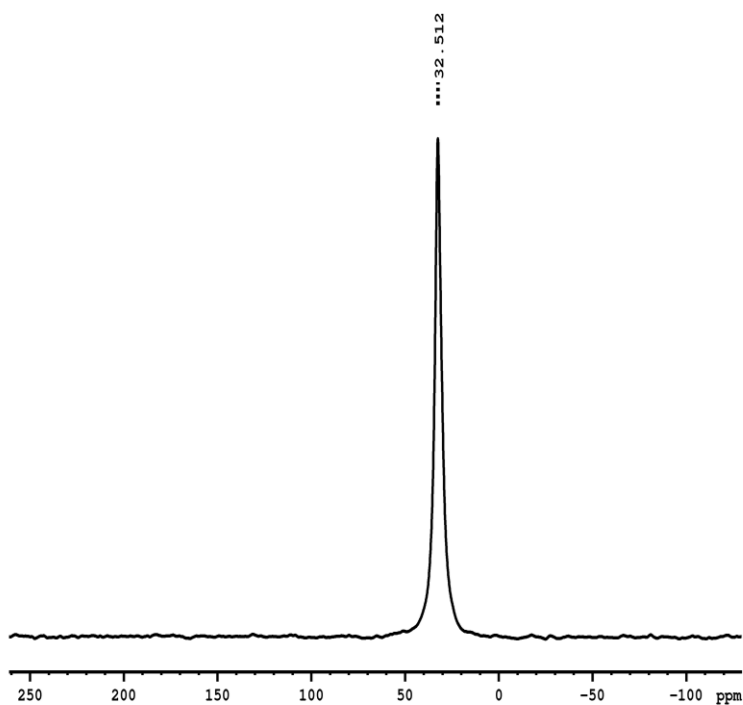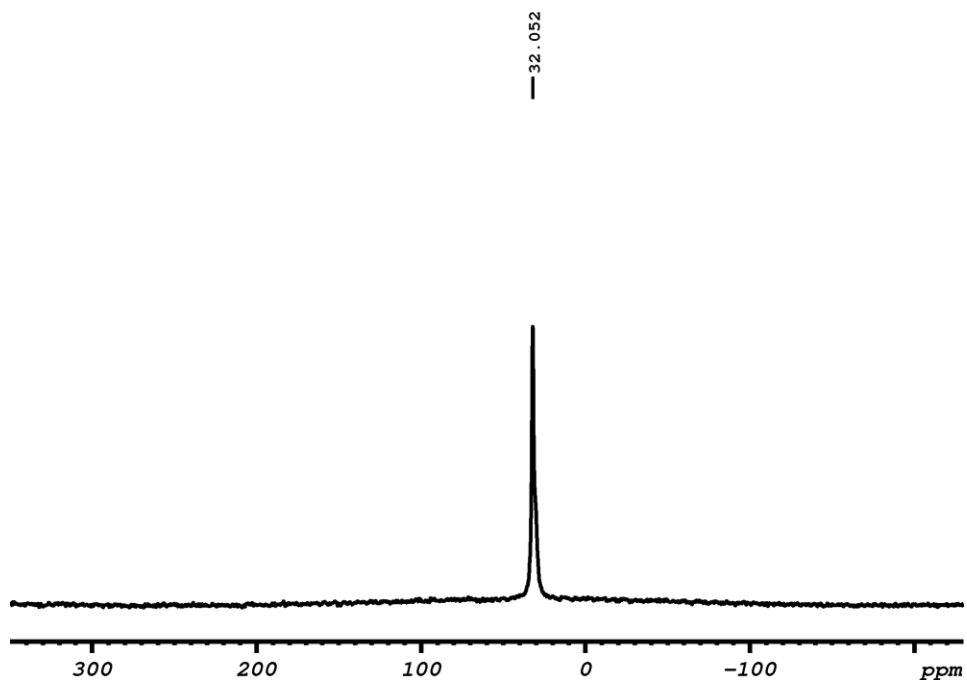

Fig. S19. ^{13}C MAS-NMR of the **(P3)** resulting from KCC-1 [($\equiv$Si−O−Si$\equiv$)(SiO)$_2$−Al−O−Ti(Np)$_3$] **3**.
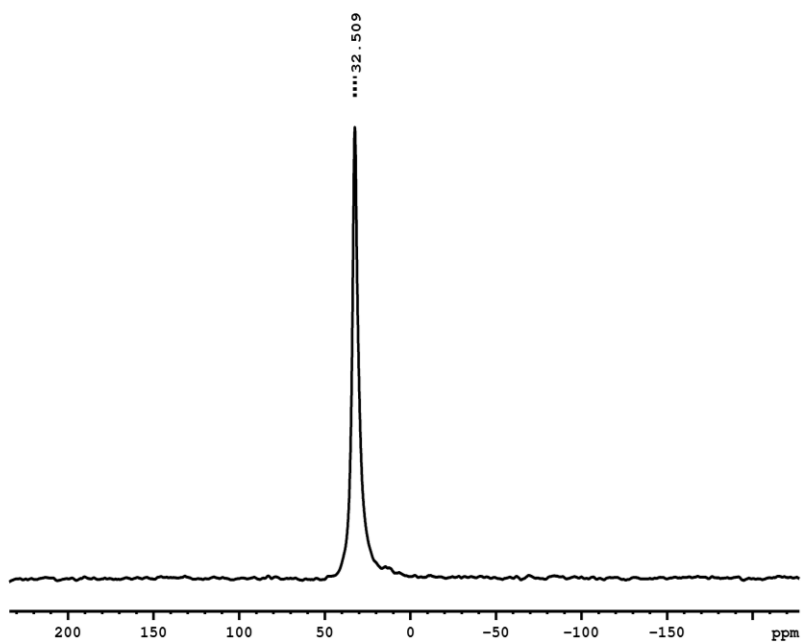
Fig. S20. ^{13}C MAS-NMR of **(P1)** resulting from KCC-1 [($\equiv$Si−O−Ti(Np)$_3$] **1.**

Fig. S21. ^{13}C MAS-NMR spectrum of the **(P5)** resulting from SBA-15 [($\equiv$Si−O−Si$\equiv$)(Si-O)$_2$Al−O−)$_2$Ti(Np)$_2$] **5.**

Fig. S22. ^{13}C MAS-NMR spectrum of **(P4)** resulting from catalyst SBA-15 [(≡Si−O−)$_2$ Ti(Np)$_2$] **4**.

Table S3. Catalysts productivities and polymer characterizations.

Catalysts/resulting polymer	Podality	Polymer	Mw (g.mol^{-1})	Productivity	PD
KCC-1-TiNp$_3$/**(P1)**	Monopodal	HDPE	989,000	14.6 g PE/mmol Ti.h^{-1}	6.7
KCC-1(-Al-O-)TiNp$_2$/**(P3)**	Monoipodal	HDPE	3,200,000	67.8 g PE/mmol Ti.h^{-1}	2.3
SBA-15 –TiNp$_3$ /**(P4)**	bipodal	LDPE	119,000	13.2 g PE/mmol Ti.h^{-1}	2
SBA-15(-Al-O-)$_2$TiNp$_2$/ **(P5)**	Bipodal	HDPE	18,000,000	44.3 g PE/mmol Ti.h^{-1}	2.7
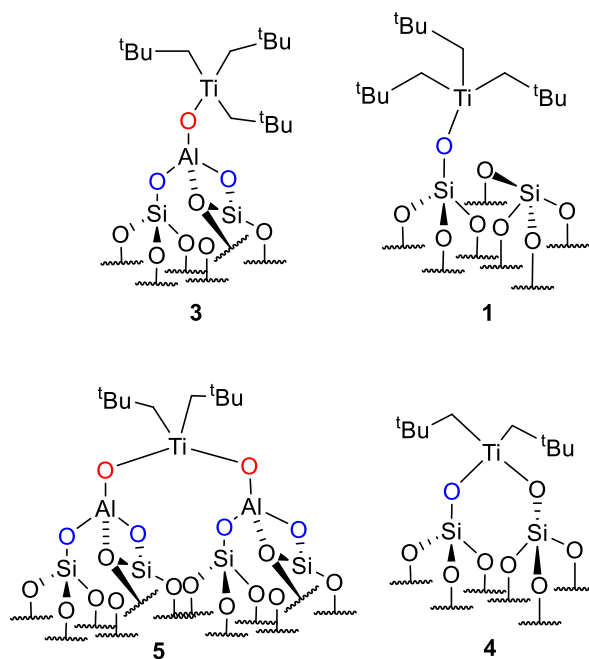
Scheme 4. Chemical illustration of all the catalysts

Table S4. NMR details of the Ti(Np)$_4$

^{1}H-NMR Signals (ppm)	Corresponded to
1.18	(Ti−CH$_2$C(C**H**$_3$)$_3$)
2.24	[Ti−C**H**$_2$C(CH$_3$)$_3$]

^{13}C-NMR Signals (ppm)	Corresponded to
34.5	[Ti−CH$_2$C(**C**H$_3$)$_3$]
37.6	[Ti−CH$_2$**C**Me$_3$]
119.6	The methylene [Ti−**C**H$_2$CMe$_3$]

Table S5. Catalysts FT-IR signals

FT-IR Signal	Corresponded to
3747 cm^{-1}	ν(OH) of [≡Si-OH]
3783 cm^{-1}	ν(OH) of [Al-OH]
2950-2869 cm^{-1}	ν[C-H] of the ^{t}Bu and ^{i}Bu
2251-2163 cm^{-1}	ν[≡Si-H] and ν[=Si-H$_2$]
1465- 1365 cm^{-1}	δ[C-H] of the ^{t}Bu and ^{i}Bu

Table S6. Catalyst **3** NMR details

^{1}H-NMR Signals (ppm)	Corresponded to
0.90	(Ti−CH$_2$C(C**H**$_3$)$_3$)/ (Ti−C**H**$_2$C(CH$_3$)$_3$)/ [≡Si−CH$_2$CH(C**H**$_3$)$_2$]
2.13	[≡Si−C**H**$_2$CH(CH$_3$)$_2$]
4.38	[Si−**H**$_x$]

^{13}C-NMR Signals (ppm)	Corresponded to
23.4	[≡Si−CH$_2$CH(**C**H$_3$)$_2$]
31.2	[Ti−CH$_2$**C**Me$_3$]/ [Ti−CH$_2$C(**C**H$_3$)$_3$]
111.6 and 132.3	The methylene [Ti−**C**H$_2$CMe$_3$]

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