

Electronic Supplementary Information

Immobilization of isolated FI catalyst on polyhedral oligomeric silsesquioxane-functionalized silica for the synthesis of weakly entangled polyethylene

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1. General experimental details

Materials. [3-t-Bu-2-O-C₆H₃CH]N(C₆F₅)₂TiCl₂ (FI catalyst) used in this work was synthesized according to the procedure reported in the literature.¹ Disilanolisobutyl polyhedral oligomeric silsesquioxane (POSS) was purchased from Hybrid Company (USA) and dried for 24h before used. 955 silica was purchased from Grace Davison Company (China). The structures of FI catalyst and POSS were shown in Fig. S1. Polymerization-grade ethylene and argon were purchased from Fangxin Ningbo Corp. (Ningbo, China) and purified by filtering through Mn molecular sieve and subsequent molecular sieve of 5 Å. Methylaluminoxane (MAO, 10 wt% solution in toluene) was purchased from Albermarle Chemical Inc. (USA). Toluene (Ningbo Chemical Reagents Co., China) was purified over sodium/benzophenone ketyl and distilled prior to use. All operations were made using Schlenk techniques or a glove box.

Support treatment. 955 SiO₂ was first treated at 200 °C for 2 h and then at 600 °C for 6 h under vacuum to ensure the removal of surface and co-intercalated water. Thermal treated SiO₂ (1.0 g) was mixed with 30 ml of toluene. MAO (3.0 ml) was added into the mixture and stirred for 4h at 60 °C. The solid was then washed by 10 ml of toluene for three times. The excess liquid was removed by evaporation to obtain the MAO-modified SiO₂.

SiO₂ functionalized by POSS. A certain amount of POSS was firstly dissolved in 10 ml of toluene for 4 h at 60 °C to achieve homogenous POSS solutions. The nominal POSS loadings are 0 wt%, 5 wt%, 10 wt% and 20 wt%, respectively. One equivalent (1.0 g) of the MAO-modified SiO₂ was mixed with 30 ml of toluene to achieve SiO₂

slurry. Then, the homogenous POSS solution was introduced into the SiO₂ slurry drop by drop. The slurry was then stirred for 24 h at 60 °C. The solid was washed by 30 ml of toluene for three times to remove any unreacted POSS and then dried under vacuum. The resultant supports were named as POSS/SiO₂-0, POSS/SiO₂-5, POSS/SiO₂-10 and POSS/SiO₂-20, respectively.

Supported FI catalyst preparation. POSS/SiO₂ support (0.5 g) was mixed with 30 ml of toluene. FI catalyst (0.2 g) was dissolved in 10 ml of toluene and then added in to the slurry of POSS/SiO₂. The slurry was stirred at ambient temperature for 24 h in the glove box for full immobilization of FI catalyst. The residual solid was washed by 30 ml of toluene for three times and dried in vacuum to achieve the immobilized FI catalyst.

Slurry ethylene polymerization. Slurry ethylene polymerization was carried out in a 1 L Buchi stainless steel autoclave reactor, equipped with a mechanical stirrer and a temperature control unit consisting of cooling water and an electric heater. The reactor was heated to 90 °C for more than 3 h and repeatedly pressurized with nitrogen, purged and evacuated (< 10 mbar) before polymerization. Then, the reactor temperature was set to 30 °C for polymerization. Toluene (500 ml) was added to the reactor. Next, 50 mg of supported catalyst was introduced into the reactor under nitrogen purging after the injection of MAO. The [Al]/[Ti] molar ratio was 1100 for each run. The polymerization then took place under a continuous ethylene flow to meet 10 bar at a stirring rate of 500 rpm. The polymerization time is 30 mins. The reactor was rapidly vented at the end of each polymerization. The obtained polymer

was precipitated and washed with acidified (*i.e.*, 2 wt % hydrochloric acid) ethanol, filtered, and dried at 50 °C under vacuum for 12 h. The conditions of homogenous reaction were as follows: 8 μmol of FI, 1100 of [Al]/[Ti] molar ratio, 500 ml of toluene, 30 °C, 10 bar and 30 min of polymerization.

Catalyst characterization. Morphology of supports (POSS/SiO₂) and catalysts (FI/POSS/SiO₂) was characterized by scanning electron microscopy (SEM; Hitachi S-4700, Tokyo, Japan). Samples were firstly pasted on the copper tap in a glove box and then sputter-coated with Pd. Energy dispersive X-ray (EDX) was also conducted on the same instrument using the EDX apparatus, in order to measure the concentration and distribution of elements. Surface elements of the supports and catalysts were measured by X-ray photoelectron spectroscopy (XPS) using a Kratos Ultra XPS system equipped with an Al K X-ray source (1486.6 eV). The samples were mounted as thin films on an adhesive copper tape in a glove box and introduced into a transfer chamber. The pressure in the analysis chamber was maintained at or below 3.0×10^{-9} torr during the measurements. The spectra were obtained at a photoelectron take-off angle of 90° measured with respect to the plane of the sample surface. Numerical analysis of the peaks was performed using the MULTIPACK software (Physical Electronics, Inc.), which evaluates the peak area and uses tables of sensitivity factors for quantitative calculation. All binding energy values were charge referenced to the Si 2p at 103.3 eV. Surface area and pore size distribution were conducted using ASAP2020-HD88 (Micromeritics Instrument Corp. USA). The data were obtained by Brunauer-Emmett-Teller (BET) method using BELSORP analysis software. Surface

imaging of supports was further measured by Scanning Probe Microscope (SPM, Veeco 3100) using tapping mode detection. The resonance frequency was 300 Hz and the elastic constants was $40 \text{ N}\cdot\text{m}^{-1}$. The Ti content in the FI/POSS/SiO₂ catalysts was measured by inductively coupled plasma (ICP, 730-ES, Varian, USA). Samples were solved in 20 ml of nitric acid (10 wt%) before analysis.

Polymer characterization. Weight-average molecular weight (M_w) and molecular weight distribution were determined using gel permeation chromatography (GPC) at 150 °C with a PL-GPC-220 instrument (Polymer Laboratories, Shropshire, U.K.), with 1,2,5-trichlorobenzene as solvent. The morphology of polyethylene was monitored by SEM. Samples were sputter-coated with Pd before the observation. Rheological studies were performed on a strain-controlled rheometer (HAAKE III instrument). A disk of 8-mm diameter was compressed under 20 tons at 120 °C for 30 min and used in all rheological studies. ² The disk between the parallel plates of the rheometer was heated to 180 °C under a nitrogen environment to prevent thermo-oxidative degradation. After thermal stabilization at 180 °C (~5 min), the rheology experiments were started. The dynamic amplitude sweep test was performed at a fixed frequency of 1 Hz to determine the linear viscoelastic regime. The dynamic time sweep test was performed to follow the entanglement formation at a fixed frequency of 1 rad/s and strain in the linear viscoelastic regime of the polymer. X-ray diffraction (XRD) measurements of nascent PE were carried out on a Bruker GADDS diffractometer with an area detector operating under 40 kV and 40 mA, using Cu K α radiation ($\lambda = 0.154 \text{ nm}$) and a step of $0.02^\circ\cdot\text{min}^{-1}$. The XRD curves were decomposed into six

components using Origin 8.5. Lorentz function was used for fitting the curves.

2. The characterization of supports (POSS/SiO₂) and catalysts (FI/POSS/SiO₂)

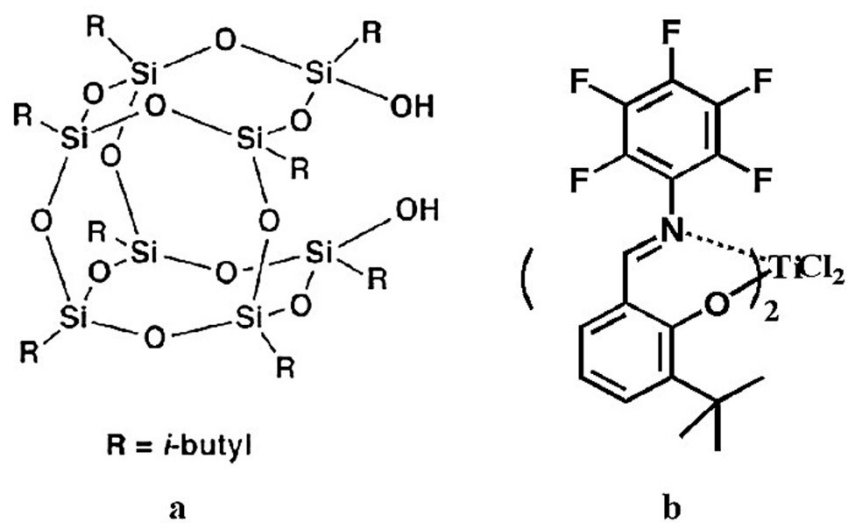


Fig. S1: Structures of POSS (a) and FI catalyst (b).

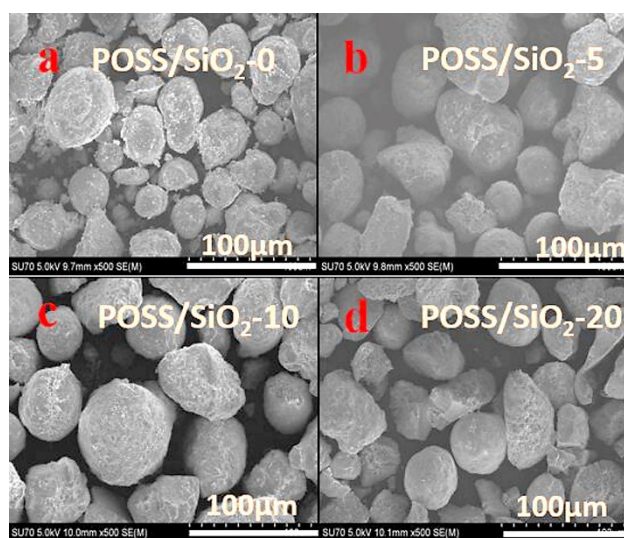


Fig. S2: Morphology of POSS/SiO₂ supports obtained from SEM: nominal POSS loadings of (a) 0 wt%, (b) 5 wt%, (c) 10 wt% and (d) 20 wt%.

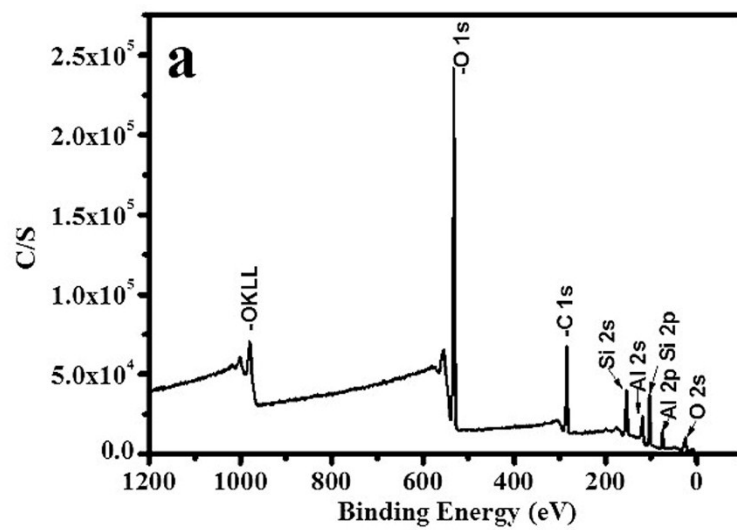


Fig. S3: Typical XPS data of supports taking POSS/SiO₂-10 as a representative.

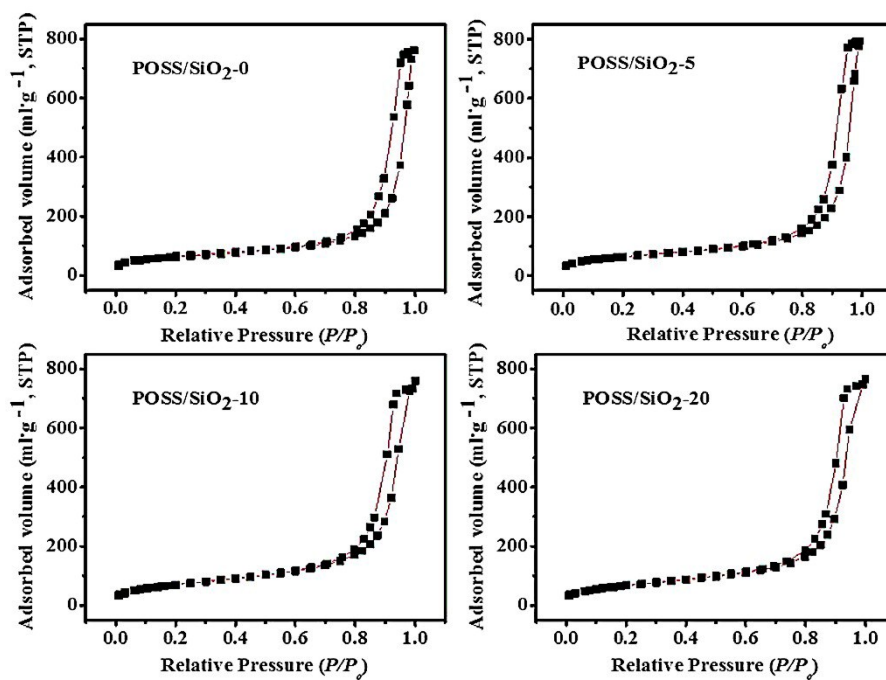


Fig. S4: Nitrogen adsorption and desorption isotherms of POSS/SiO₂ supports.

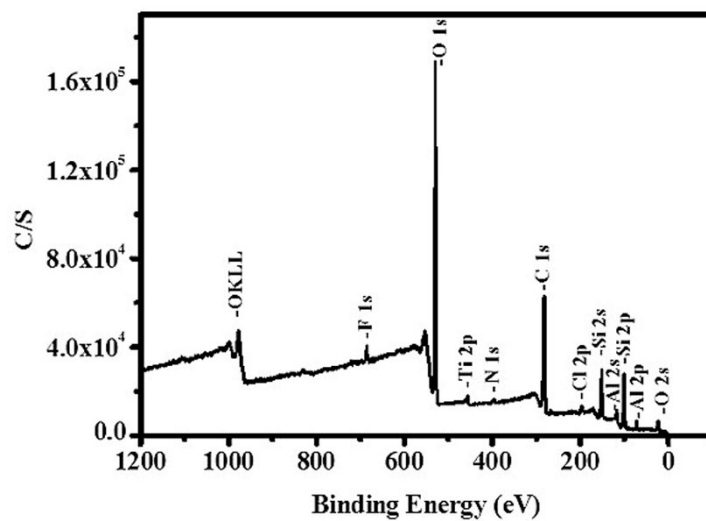


Fig. S5: Typical XPS data of immobilized FI on supports taking FI/POSS/SiO₂-10 as a representative.

3. The characterization of produced polymers

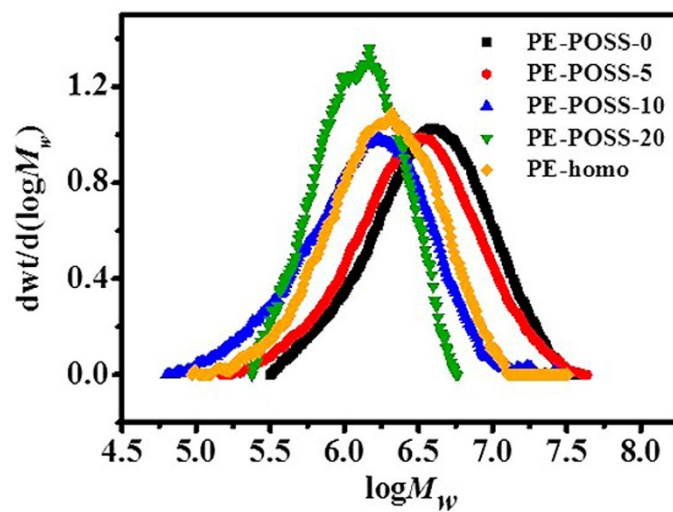


Fig. S6: GPC curves of the synthesized UHMWPE.

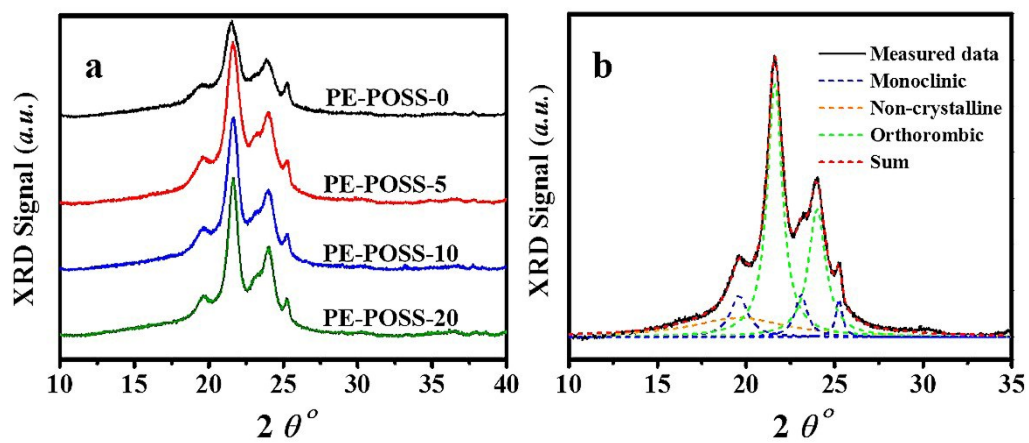


Fig. S7: The XRD patterns of the synthesized PE (a) and fitting curves of PE-POSS-10 (b).

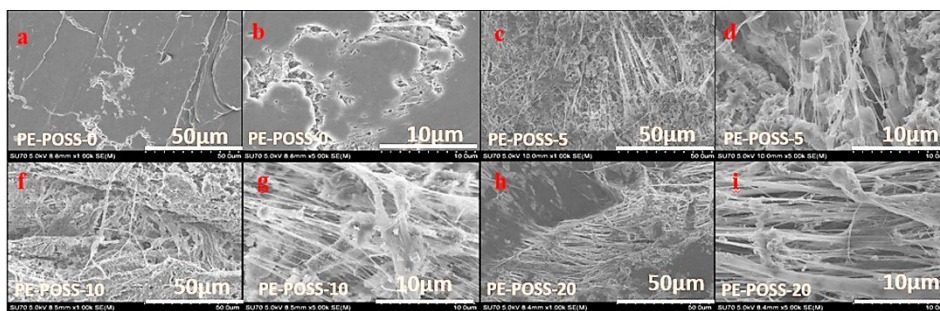


Fig. S8: Morphology of the synthesized polymers from SEM analysis.

The SEM morphology of the nascent polymers is shown in Fig. S8. String structures can be noticed particularly in the polymer with weakly entangled state. The strings increase in popularity when the POSS fraction is increased to 10 wt%. The PE-POSS-10 contains a large amount of strings. However, the strings become less in the matrix of PE-POSS-20. The formation of string morphology may be due to that the polymerization is conducted at low temperature (*i.e.*, 30 °C), where polymer chains can be crystallized as soon as they are growing out, generating the orientation of polymer chains.^{3,4} The increase of string numbers indicates that a less number of entangled chains.^{3,4}

4. Tables:

Table S1: Results obtained from XPS Analysis for the POSS/SiO₂ supports

	X_{Si2p} (wt%) ^a	X_{Al2p} (wt%) ^a	$f_{Si,surf-POSS}$ (%) ^b	X_{POSS} (wt%) ^b
POSS/SiO ₂ -0	14.8	17.5	5.9	/
POSS/SiO ₂ -5	20.3	10.2	10.3	3.5
POSS/SiO ₂ -10	19.9	6.8	17.1	8.7
POSS/SiO ₂ -20	26.5	8.5	14.2	8.6

^a X_{Si2p} and X_{Al2p} is the mass concentration of Si 2*p* and Al 2*p* in the POSS/SiO₂ support.

^b $f_{Si,surf-POSS}$ is the fraction of Si_{101.9 eV} (*i.e.*, Si atoms at the external surface). This value is obtained by peak deconvolution of Si 2*p*. X_{POSS} is the loading of POSS, which is calculated as follows:

$$X_{POSS} = X_{Si2p} \times (f_{Si,surf-POSS} - f_{Si,surf-0}) \times 874 / (28 \times 8)$$

where $f_{Si,surf-0}$ is the fraction of Si_{101.9 eV} of the POSS/SiO₂-0 (*i.e.*, 5.9%); 878 (g·mol⁻¹) and 28 (g·mol⁻¹) are the molar mass of POSS and Si, respectively.

Table S2: XPS results of the FI/POSS/SiO₂ catalysts

Samples	BE (eV) Ti 2 <i>p</i> _{3/2}	BE (eV) Ti 2 <i>p</i> _{1/2}	BE(eV) Al 2 <i>p</i>	BE (eV) Al 2 <i>p</i> ^a
Homogenous FI	455.7	461.7	-	-
FI/POSS/SiO ₂ -0	456.7	462.7	72.6	74.1
FI/POSS/SiO ₂ -5	456.7	462.7	72.7	74.8
FI/POSS/SiO ₂ -10	456.7	462.7	72.7	75.2
FI/POSS/SiO ₂ -20	457.1	463.2	72.9	75.2

^a XPS results (Al 2*p*) of the corresponding POSS/SiO₂ supports.

Table S3: Fitting results of XRD patterns

Samples	$X_{o,XRD}\%$ ^a	$X_{m,XRD}\%$ ^b	$X_{c,XRD}\%$ ^c	Monoclinic (nm)		
				$n_{25.3^\circ}$	$n_{23.4^\circ}$	$n_{19.5^\circ}$
PE-POSS-0	48.4	13.2	61.6	24.4	10.5	8.1
PE-POSS-5	54.2	13.6	67.8	22.9	10.5	7.3
PE-POSS-10	64.8	15.8	80.7	19.7	10.3	7.0
PE-POSS-20	50.3	10.9	61.3	25.6	14.5	7.5

^aThe fraction of orthorhombic phase; ^bThe fraction of monoclinic phase, ^cThe crystallinity of polymers.

[Table S3](#) shows the fitting results of XRD patterns of nascent PE. The XRD patterns and fitting curves are shown in [Fig. S7](#). The diffraction at 21.6° and 24.0° can be attributed to the orthorhombic unit cell structure of the (110) and (200) reflection planes of the PE. The reflection at 19.5° with narrow width, 23.2° and 25.2° can be ascribed to the monoclinic unit cell structure of the (010), (200) and (210) planes, respectively. The reflection at 19.5° with broad width corresponds to the amorphous phase.⁵

5. References

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