

Electronic Supplementary Information

A robust immobilization strategy in the nano-dispersed Ziegler-Natta catalyst: noncovalent O-Ti coordination

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General experimental details

Materials. All the operations on moisture-sensitive and air-sensitive materials were performed with the protection of an inert nitrogen atmosphere or in a glovebox. Disilanolisobutyl POSS (POSS-2OH) and octalsobutyl POSS (oct-POSS) were purchased from Changsha Baxi Company and dried for at least 24 h. The anhydrous magnesium chloride (MgCl_2) was offered by Sinopec Tianjin Branch, which was stored in the glovebox. TiCl_4 with the concentration of 99.9 wt% was purchased from J&K Chemical Corp. The cocatalysts (i.e., triethylaluminium (TEA), triisobutylaluminum (TIBA), tri-*n*-hexylaluminum (THA) and trioctylaluminum (TOA)) with the concentration of 1 mol/l were purchased from J&K Chemical Corp. Analytical tetrahydrofuran (THF), toluene, *n*-hexane, *n*-heptane, were purified through the dehydration column equipped in the solvent refining system (Innovation Tech., USA, MD-5).

Catalyst Preparation. 3.5 g of POSS-2OH or oct-POSS was solved into 60 ml of THF at 30 °C and stirred for 1 h. In order to make the MgCl_2 molecules occupying the surface of POSSs, 0.3 g of MgCl_2 was added into the POSS solution and the mixture were stirred at 120 °C for 4 h. The solution was removed by vacuum for 4 h at 60 °C to achieve solids. Then the solids were dissolved into 50 ml of *n*-hexane and stirred at 60 °C for at least 12 h. The unsolvable solids (extra MgCl_2) were further removed by filtration, leaving the residual transparent solution for further reaction. 9 mmol of TiCl_4 was added into the solution drop-wisely at 60 °C, where the yellowish solids were gradually precipitated from the solution after 4 h. The solid was further washed by *n*-hexane 3 times and dried under vacuum for 6 h to achieve the solid catalysts (named as POSS-2OH/ MgCl_2 - TiCl_4 and oct-POSS/ MgCl_2 - TiCl_4 , respectively). The POSS-2OH/ TiCl_4 catalysts were synthesized with the equal stoichiometry in the *n*-hexane and used as a benchmark catalyst. This catalyst was in the homogeneous state owing to the good solubility of POSS-2OH in the *n*-hexane. Classical

MgCl₂ immobilized TiCl₄ (MgCl₂-TiCl₄) catalyst was synthesized as following as also a benchmark catalyst. 1.0 g of MgCl₂ was dissolved into the 50 ml of THF at 120 °C for 2 h. A solid would be obtained after the THF was removed by vacuum. 100 ml of *n*-hexane was mixed with the dried solid followed the introduction of 1.0 ml of TiCl₄, stirring for 4h. The solid was washed by the *n*-hexane three times. The catalyst was achieved after the solid was dried in the vacuum at 60 °C for 4 h.

Ethylene polymerization. Ethylene polymerization was conducted in a 1.0 l Buchi stainless steel autoclave reactor. The reactor was heated and kept over 130 °C under vacuum for more than 3 h. Then the reactor was cooled to 60 °C and repeatedly replaced with ethylene before polymerization. 350 ml of *n*-heptane was added to the reactor. After the introduction of TEA as the cocatalyst, 0.025 mmol of TiCl₄ was injected into the reactor. The polymerization was conducted under a continuous ethylene flow up to 10 bars at a stirring rate of 450 rpm, where the consumption rate of ethylene was recorded by a mass flow meter to trace the polymerization kinetics. Each run was stopped after 60 mins of polymerization following with the introduction of acidified ethanol. The synthesized polymers were washed by massive ethanol and dried at 60 °C under vacuum for 24 h.

Density functional theory (DFT) calculations. The DFT calculations performed in the present work used 6-31G* basis set and ωB97XD exchange-correlation functional. The geometric optimization and the vibrational frequency calculations used eigenmode-following based algorithm and analytic gradient, respectively, as usually implemented in quantum chemistry software package. To reduce the computational effort, *i*-butyl side chains of the POSS-2OH or oct-POSS were replaced by H atoms. The geometric optimizations were usually performed from multiple starting geometries to obtain stable structures. The calculated vibration frequencies of CO were calibrated according to the experimental data. In detail, the calculated frequency of gas phase

CO molecule, 2244 cm^{-1} , was aligned to the experimentally determined physical adsorption frequency, 2131 cm^{-1} , and all the other CO frequencies on different adsorption sites were shifted accordingly. All the calculations were performed with GAUSSIAN09 package.² The calculations of CO adsorption on/in POSS molecules (without Mg and Cl) were well described by using 6-31G* basis set. The results by using $\omega\text{B97XD}/6\text{-}31\text{G}^*$ showed a fairly good agreement with the experimental data, as demonstrated in the text.

Characterization. The morphology of catalysts was observed by using a scanning electron microscopy (SEM, Hitachi S-4700, Japan), where the samples were sputter-coated by Pt for 1 mins before the observation. The morphology and elemental distribution of catalytic nanoparticles were further studied by the transmission electron microscopy (Talos F200X, Thermo-Fisher) under HAADF-STEM mode and energy dispersive X-ray detector (EDX), respectively. For the preparation of observed nanoparticles, 10 mg of catalyst was dispersed in 30 ml of *n*-hexane and ultra-sounded for 15 mins. One droplet of the suspension was set on the copper screen and dried in the glove box. The crystal structures of the catalytic nanoparticles, POSS-2OH and MgCl_2 were measured by X-ray diffraction (XRD, Bruker GADDS diffract meter), operated at 40 kV, 40 mA and 0.02° of step size with the Cu $K\alpha$ radiation. The binding energy (BE) of the Ti $2p$ and O $1s$ orbitals in the catalysts were investigated by X-ray photoelectron spectroscopy (XPS) measurements. All catalysts were mixed with the cocatalyst (e.g., TEA) in advance and dried by the vacuum. The obtained solids were transferred into the XPS bin under the protection of nitrogen. The XPS measurements were carried out on Escalab 250Xi, where the Al $K\alpha$ radiation was used as the X-ray source (300 W, 1486.3 eV) and the vacuum was maintained at 5×10^{-9} Torr. The BE was calibrated to C1s peak (i.e., 284.6 eV). The composition of Ti $2p$ spectra was acquired according to the Gaussian fitting. CO *in-situ* FTIR measurement was conducted at low temperature

(-180 °C), where the concentration of CO was 10% in He and the pressure was varied between 1.0-1.5× 10⁻³ mbar. The spectra were taken after each pulse. The concentration of titanium in the synthesized catalyst was characterized by a ultraviolet-visible (UV-vis) spectrum according to the hydrogen peroxide colorimetric method. The catalysts were dissolved in 2 ml of H₂O₂ and 5 ml of H₂SO₄ solution (1 mol·l⁻¹) for 12 h to achieve a transparent solution. This solution was diluted with the H₂SO₄ solution to 25 ml. The UV-vis spectra were recorded by a TU-1901 spectrophotometer (PERSEA Corp, China). The bulk concentration of MgCl₂ in the catalytic nanoparticles were measured by inductively coupled plasma (ICP, 730-ES, Varian, USA). The average molecular weight (M_w) and its distribution (MWD) were investigated by a gel permeation chromatography (GPC, Polymer Laboratories, Shropshire, U.K.). 1,2,4-trichlorobenzene was used as the mobile phase at 150°C. The melting point and crystallinity of the synthesized polymer were measured by differential scanning calorimeter (DSC, DSC-7 equipment, PerkinElmer Corp., USA). 6-8 mg of polymer was heated from 50 °C to 160 °C and then maintained for 3 mins. This sample was further cooled to 50 °C followed by the same heating program. The heating and cooling rate were kept for 10 °C·min⁻¹. T_m^1 and X_c^1 were denoted as the melting point and crystallinity of the polymer during the first heating scan. T_m^2 and X_c^2 were the same characterization for the second heating scan.

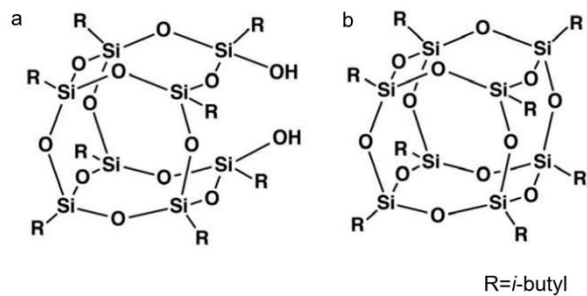


Fig. S1 The chemical structures of POSS-2OH (a) molecules and oct-POSS (b).

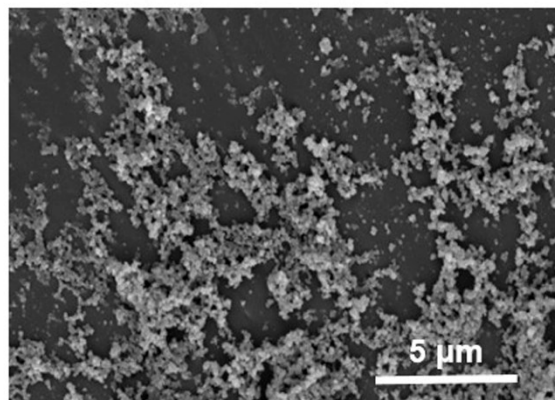


Fig. S2 SEM Morphology of the dried particles after the POSS-2OH/MgCl₂-TiCl₄ catalyst dispersing in the *n*-hexane.

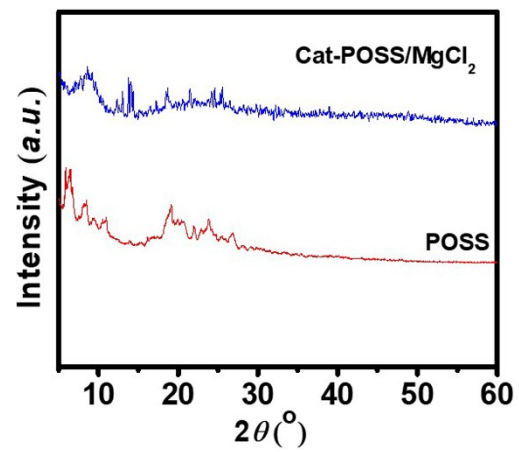


Fig. S3 XRD spectra of the POSS-2OH/MgCl₂-TiCl₄ catalyst and POSS-2OH aggregates.

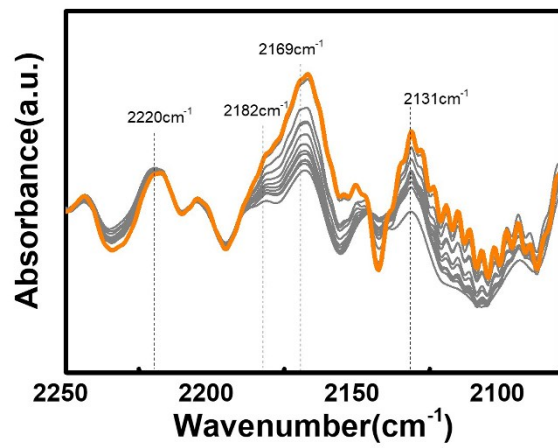


Fig. S4 CO in-situ FTIR spectra of oct-POSS.

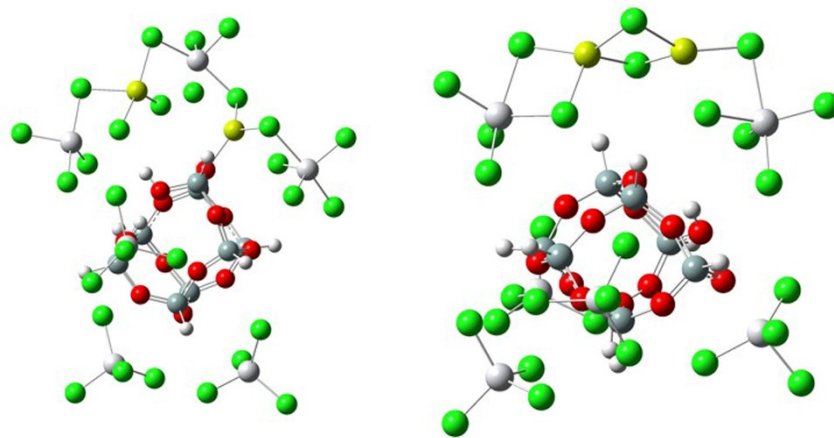


Fig. S5 Two optimized structure of model cluster containing 1 POSS-2OH, 2 MgCl₂ and 6TiCl₄, showing the close binding between MgCl₂ and TiCl₄.

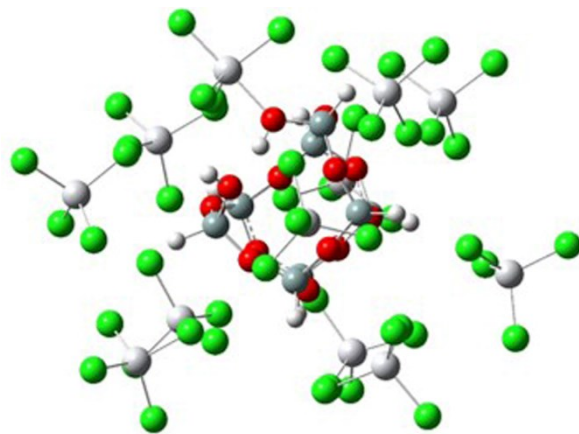


Fig. S6 Geometry optimizations of multiple TiCl₄ molecules on POSS surface.

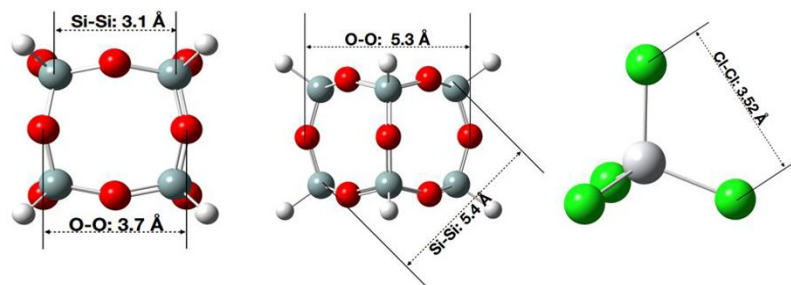


Fig. S7 Comparison of molecular sizes between TiCl_4 and POSS.

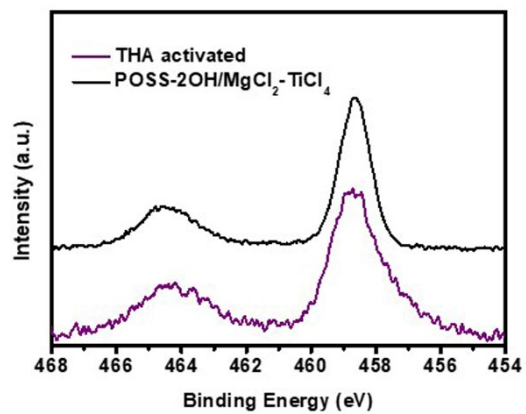


Fig. S8 Typical Ti 2*p* XPS curves of POSS-2OH/MgCl₂-TiCl₄ catalyst after the activation of cocatalyst.

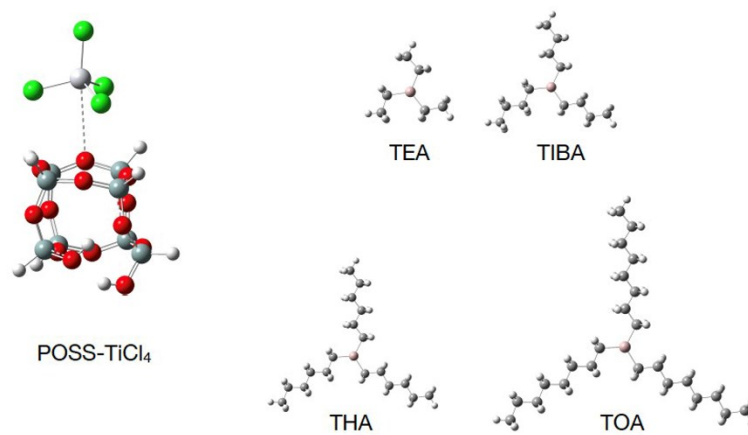


Fig. S9 Molecular structures used for frequency calculation shown in Figure 5.

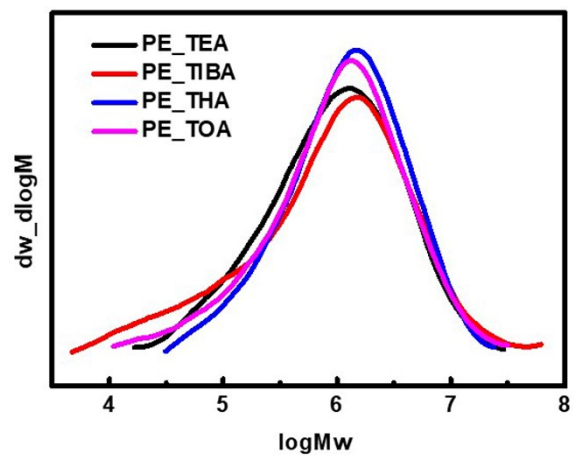


Fig. S10 The GPC curves of the polymers synthesized by the POSS-2OH/MgCl₂-TiCl₄ catalyst.

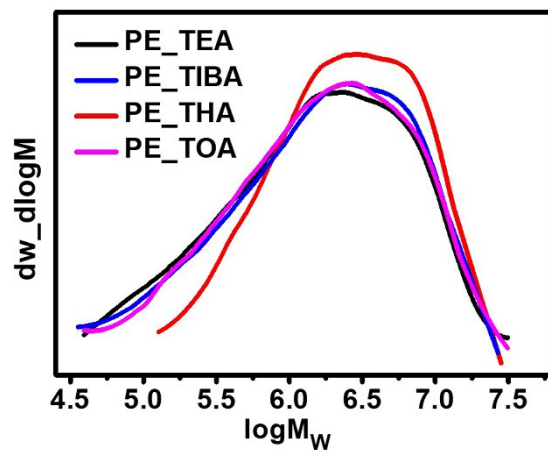


Fig. S11 GPC curves of the polymers synthesized by the oct-POSS/MgCl₂-TiCl₄ catalyst.

Table S1 The surface and bulk concentration of Mg and Ti atoms in the POSS-2OH/MgCl₂-TiCl₄ catalyst.

Elements	STEM-EDX/surface wt %	ICP/bulk wt %
Mg atoms	0.6	0.13
Ti atoms	30.6	12.0

Table S2 The crystallinity and melting point of the synthesized polyethylene

PE	Cocatalyst	T_1 (°C)	Tm_1 (%)	T_2 (°C)	Tm_2 (%)
PE-POSS-2OH/ MgCl ₂ -TiCl ₄	TEA	143.5	66.1	137.4	51.9
	TIBA	144.7	64.4	136.7	48.0
	THA	144.6	66.2	136.8	49.6
	TOA	143.7	66.1	136.4	49.2
PE-Oct-POSS/ MgCl ₂ -TiCl ₄	TEA	144.4	71.9	137.7	56.9
	TIBA	145.0	67.6	137.9	51.4
	THA	145.1	68.6	137.7	53.0
	TOA	145.3	71.3	137.6	55.0

References

1. Y.M. Chen, P. Liang, Z. Yue, W. Li, C.D. Dong, B.B. Jiang, J.D. Wang, Y.R. Yang. *Macromolecule*, 2019, **52**, 7953.
2. E. Breuza, G. Antinucci, P.H.M. Budzelaar, V. Busico, A. Correa, C. Ehm. *J. Phys. Chem. C*, 2018, **122**, 9046.